NEW AMINO- AND TITANOXYCARBENE COMPLEXES OF GROUP 6 METALS

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I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Summary

This study comprised the synthesis of new aminocarbene complexes of group 6 metals as well as a new titanoxychromium carbene complex.

The reaction of 2-benzothiazolyllithium with chromium hexacarbonyl followed by alkylation with methyl triflate and aminolysis with ammonia afforded the complex $[(CO)_5Cr{=}C(NH_2)\overline{CNC_6H_4S}\text{-}o]$.

Fischer-type carbene complexes were prepared according to the Fischer-method but alkylated with trimethyloxonium tetrafluoroborate. Aminolysis of these complexes with 2-amino-thiazoline and 2-aminobenzothiazole unexpectedly yielded the complexes $[(CO)_5W{=}C(Ph)N\overline{C{=}NHC_2H_4S}]$, $[(CO)_5Cr{=}C(Me)N\overline{C{=}NHC_6H_4S}\text{-}o]$, $[(CO)_5Cr{=}C(Ph)N\overline{C{=}NHC_6H_4S}\text{-}o]$ and $[(CO)_5Mo{=}C(Ph)N\overline{C{=}NHC_6H_4S}\text{-}o]$, wherein a hydrogen atom has migrated from one nitrogen atom to another. Single crystal X-ray crystallography was used to determine the molecular structure of $[(CO)_5W{=}C(Ph)N\overline{C{=}NHC_2H_4S}]$. It was found that intermolecular hydrogen bonding occurs in the solid state and that the molecular units are essentially dimeric. No similar complexes have been described in the literature to date.

The reaction of chromium hexacarbonyl with phenyllithium yields a lithium salt which can be converted to a crystalline ammonium salt $[(CO)_5Cr{=}C(Ph)O]^-[NEt_4]^+$. The reaction of this salt with (bis(cyclopentadienyl))titanium dichloride in the presence of silver tetrafluoroborate yields $[(CO)_5Cr{=}C(Ph)OTiCp_2Cl]$. The molecular structure of this complex was determined by single crystal X-ray crystallography. The structure of this complex does not differ significantly from already known structures containing different organic groups on the carbene carbon. The linear orientation of

the carbene carbon, the oxygen bound to it and the titanium unit may indicate delocalised π-interaction.

Opsomming

Hierdie studie het die sintese van nuwe aminokarbeenkomplekse van die groep 6 metale asook 'n nuwe titanoksiechroomkarbeenkomples behels.

Die reaksie van 2-bensotiasoliellitium met chroomheksakarboniel, gevolg deur alkilering met metieltriflaat en aminolise met ammoniak lewer die kompleks $[(CO)_5Cr{=}C(NH_2)\overline{CNC_6H_4S}\text{-}o]$.

Fischer-tipe karbeenkomplekse is berei volgens die Fischer-metode en gealkileer met trimetieloksoniumtetrafluoroboraat. Amminolise van hierdie komplekse met 2-amino-2-tiasolien en 2-aminobensotiasool lewer onverwags die komplekse $[(CO)_5W{=}C(Ph)N\overline{C{=}NHC_2H_4S}]$, $[(CO)_5Cr{=}C(Me)N\overline{C{=}NHC_6H_4S}\text{-}o]$, $[(CO)_5Cr{=}C(Ph)N\overline{C{=}NHC_6H_4S}\text{-}o]$ en $[(CO)_5Mo{=}C(Ph)N\overline{C{=}NHC_6H_4S}\text{-}o]$, waar 'n waterstofatoom migreer het van een stikstofatoom na 'n ander. Die molekulêre struktuur van $[(CO)_5W{=}C(Ph)N\overline{C{=}NHC_2H_4S}]$ is bepaal met behulp van enkelkristal X-straal kristallografie. Dit is gevind dat intermolekulêre waterstof-binding plaasvind in die vaste toestand en dat die molekulêre eenhede eintlik dimeries is. Geen soortgelyke komplekse is tot dusver in die literatuur gerapporteer nie.

Die reaksie van chroomheksekarboniel met feniellitium lewer 'n litiumsout wat omgeskakel kan word na 'n kristallyne ammoniumsout $[(CO)_5Cr{=}C(Ph)O]^-[NEt_4]^+$. Reaksie van hierdie sout met (bis(siklopentadieniel))titaandichloried in die teenwoordigheid van silwertetrafluoroboraat lewer $[(CO)_5Cr{=}C(Ph)OTiCp_2Cl]$. Enkelkristal X-straal kristallografie is gebruik om die struktuur van hierdie kompleks te bepaal. Die struktuur van hierdie kompleks verskil nie noemenswaardig van bekende komplekse in die literatuur nie. Die lineêre oriëntasie van die

karbeenkoolstof, die suurstof daaraan gebind en die titaaneenheid mag dui op gedelokaliseerde π-interaksie.

The striving for wisdom is the second paradise of this world.

- Paracelsus

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Abbreviations

Å		Ångstrom (10^{-10} m)
Bu^t		Tertiary buthyl
Cp		Cyclopentadienyl
Cp'		Methyl cyclopentadienyl
Cp*		Pentamethyl cyclopentadienyl
Et		Ethyl
IR		Infrared
MAO		Methyl aluminoxane
Me		Methyl
NMR		Nuclear magnetic resonance spectroscopy
Pr		Propyl
Pr^i		Isopropyl
R		Alkyl or aryl group
THF		Tetrahydrofuran
IR:	m	Medium
	sh	Shoulder
	st	Strong
	w	Weak
NMR:	δ	Chemical shift
	m	Multiplet
	s	Singlet
	t	Triplet

Chapter 1

Introduction and aims of the study

1.1 General Introduction

The discipline of chemistry has a long and curious history, more rooted in myth and superstition than most branches of science. The practice of chemistry dates back to antiquity, with the roasting of meat, dying of wool and brewing of beer. The first attempt at explaining the nature of matter came with the atomic theory of Democritus around 600 B.C. However, more distinguished philosophers such as Plato and Aristotle dismissed this idea as being too speculative and atomism lay in limbo for about 2000 years. Meanwhile, the alchemists of Egypt and Arabia continued the practice of chemistry. Although alchemy today is regarded with disdain, the alchemists did make a significant contribution to the basic chemical knowledge still used today. They discovered many elements as well as indispensable chemicals such as sulphuric acid. Today the production of sulphuric acid is used as index of a country's industrialisation. Alchemy was practiced in Europe throughout the Dark Ages and even Isaac Newton was reputed to have been an alchemist.

The advent of modern chemistry was Joseph Priestley's discovery of oxygen and the developments that went with it. Since the 1830s chemistry and physics became de-

marcated disciplines and different fields of specialisation became established within chemistry, such as organic chemistry and physical chemistry.[1]

The first known organometallic compound was isolated in the early 19th century.[2] Since Zeise's discovery of his eponymous salt, an organometallic compound has come to be known as any compound with a metal-carbon σ-bond, although several compounds containing only so-called half-metals such as boron or arsenic are also classified as organometallic compounds due to their similar chemical behaviour.[3] The discovery of ferrocene[4] in the 1950s caused an explosion in the field and since then organometallic chemistry has experienced rapid growth, with many applications in industrial catalysis, organic synthesis and, more recently, in biological chemistry.

1.2 Metal carbonyl complexes

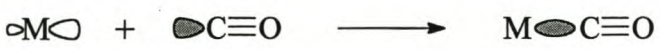
Since all the new compounds in this study have been prepared using a metal carbonyl complex as starting material, it is appropriate to say something about metal carbonyl complexes in general at this point. Metal carbonyl complexes occur as mono- or binuclear complexes as well as cluster compounds. They can be homo- or heteronuclear, and the carbonyl ligands can be terminal or bridged. All the metal carbonyl complexes that were used during this study were mononuclear and contained only terminal carbonyl ligands. Metal carbonyls of this kind are all hydrophobic liquids or volatile sol-

[1] M. J. Nye, *From Chemical Philosophy to Theoretical Chemistry*, University of California Press, Berkeley, 1993.
[2] W. C. Zeise, *Ann. Phys.*, 1827, **40**, 234.
[3] N. J. Long, *Metallocenes: An Introduction to Sandwich Complexes*, Blackwell Science, Oxford, 1998.
[4] (a) T. J. Kealy and P. L. Paulson, *Nature*, 1957, **168**, 1039. (b) S. A. Miller, J. A. Tebbeth and J. F. Tremaine, *J. Chem. Soc.*, 1952, 632.

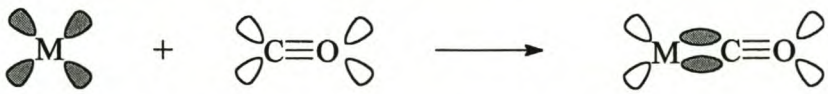
ids, soluble to variable degrees in non-polar solvents. The M-C-O chains are linear, and with the exception of $V(CO)_6$, these compounds all obey the 18-electron rule.[5]

There are many varied ways of synthesizing metal carbonyls. The obvious route - direct reaction of a metal with CO - works only for nickel and iron.[5] All other metal carbonyls are prepared from metal compounds under reductive conditions with sodium[6] or aluminium alkyls[7] and carbon monoxide or a carbon monoxide/hydrogen mixture. The group 6 carbonyls [$Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$] constitute the only complete family of metal carbonyls that are stable and in common use.

A π-acceptor ligand is one which accepts π-electron density from a metal into an empty π- or π*-type orbital of its own (e. g. an empty p-orbital). Carbon monoxide is a prime example of a π-acceptor ligand. The bond between carbon monoxide and a metal is a synergic one, consisting of two mutually dependent components (Figure 1.1).



(a) Carbon to metal bonding



(b) Metal to carbon back donation

Figure 1.1

Firstly, there is the overlap of the filled carbon σ-orbital with a σ-type metal orbital. However, this dative bond leads to an unstable concentration of electron density at the

[5] F. A. Cotton and G. Wilkinson, *Advanced Organometallic Chemistry, 5th Edition*, John Wiley and Sons, New York, 1988.
[6] F. Calderazzo and G. Pampaloni, *J. Organomet. Chemistry*, 1983, **250**, C33.

metal centre, especially if the metal is in an oxidation state lower than +2. Therefore the metal pushes some of the excess electron density back to the ligand if the ligand has suitable acceptor orbitals. In the case of carbon monoxide, this so-called back donation occurs via dative overlap of a filled d_π-orbital or dp_π-hybrid orbital, to an empty orbital of the carbonyl ligand.[8] This can be an empty p-orbital according to valence bond theory or a π^*-antibonding orbital if the molecular orbital approach is taken. It is easy to see that this kind of bonding stabilises metals in low oxidation states, and this is why many organometallic compounds are synthesized with carbonyl ligands. This phenomenon is also seen in the case of carbene complexes, and the carbene complexes in this study are all pentacarbonyl complexes of group 6 metals.

1.3 Metal carbene complexes

(i) Introduction

The first planned synthesis of a carbene complex was done in 1964.[9] However, it is possible that the first metal carbene complex was prepared as long ago as 1915,[10] although it was not realised at the time. Today carbene complexes play an important role in catalysis[11] and organometallic and organic synthesis,[12] and several excellent

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[7] (a) F. Calderazzo and R. Poli, *Gazz. Chim. Ital.*, 1985, **115**, 573. (b) R. A. Walton, *ACS Symp. Ser.*, 1981, **155**, 212.

[8] F. A. Cotton and G. Wilkinson, *Advanced Organometallic Chemistry, 5th Edition*, John Wiley and Sons, New York, 1988.

[9] E. O. Fischer and A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, 1964, **3**, 580.

[10] L. Chugaev and M. Skanavy-Grigorizeva, *J. Russ. Chem. Soc.*, 1915, **47**, 776.

[11] (a) S. K. Armstrong, *J. Chem. Soc. Perkin Trans. I*, 1998, **168**, 1. (b) M. Schuster and S. Blechert, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2037. (c) M. P. Doyle, J. H. Griffin and J. Conceicao, *J. Chem. Soc., Chem Commun.*, 1985, 328.

[12] (a) J. Barluenga, *Pure Appl. Chem.*, 1999, **71(8)**, 1385. (b) L. S. Hegedus, *Tetrahedron*, 1997, **53(12)**, 4105. (c) J. Barluenga, *Pure Appl. Chem.*, 1996, **68(3)**, 543. (d) F. Z. Dörwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, New York, 1999.

review articles testify to this.[13] The majority of known carbene complexes are neutral and mononuclear with a single terminal unidentate carbene ligand. The carbene carbon is sp^2-hybridised. Bridged carbene ligands also exist.[13(a)] This discussion will focus mainly on the Fischer-type carbene complexes of the group 6 metals.[14] In discussing the synthesis of carbene complexes and their reactions, special attention will be paid to reactions that are similar to those utilised in this study.

(ii) Synthesis

Although there are many ways of synthesizing metal carbene complexes, the preparation by Fischer *et al.*[15] and variations thereof, remains the most commonly employed method due to its relative ease and good yield. According to Fischer's method, the metal carbonyl is treated with an organolithium reagent to generate an anionic acyllithium salt. The lithium salt is converted to an ammonium salt that is methylated by CH_2N_2 (Scheme 1.1) after acidification. Later on, it was found that direct alkylation of the lithium salt with alkyloxonium tetrafluoroborate is easier and give higher yields (Scheme 1.2).[16] This is the method used to prepare all the precursor carbene complexes in this study. Methyl triflate has proved to be a useful methylating reagent too.[17]

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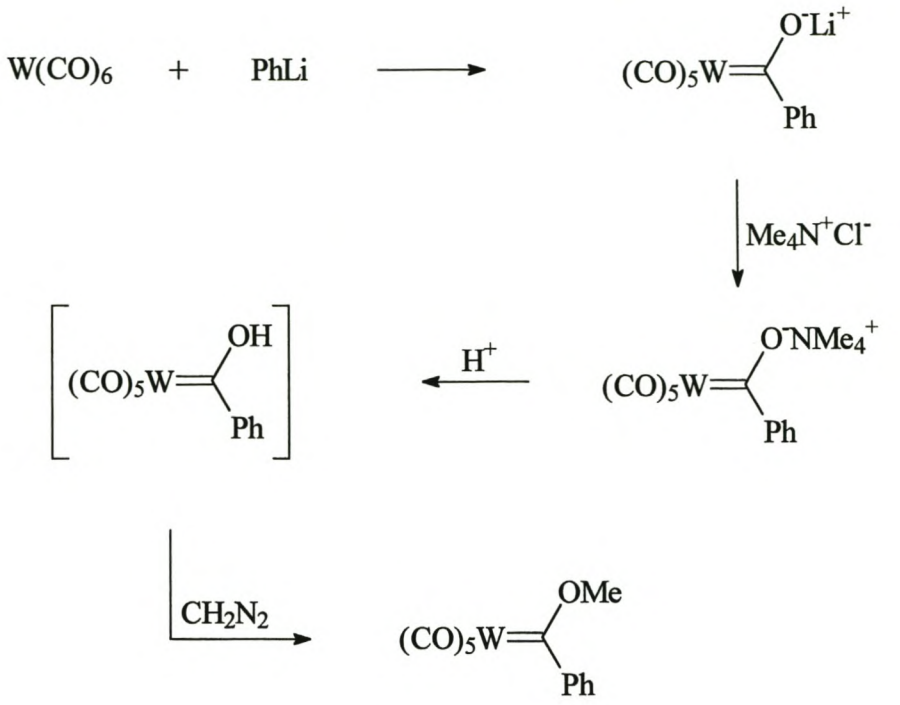
[13] (a) D. J. Cardin, B. Çetinkaya and M. F. Lappert, *Chem. Rev.*, 1972, **72(5)**, 545, (b) F. J. Brown, *Prog. Inorg. Chem.*, 1980, **27**, 1, (c) G. Wilkinson, F. G. A. Stone, E. W. Abel, *Comprehensive Organometallic Chemistry*, 1982, **3**, p.155. (d) M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 44. (e) D. F. Harvey and D. M. Sigano, *Chem. Rev.*, 1996, **96**, 271. (f) W. D. Wulff, *Organometallics*, 1998, **17**, 3116. (g) K. H. Dötz and J. Pfeiffer, *Transition Met. Org. Synth.* 1998, **1**, 335. (h) W. A. Herrmann, F. J. Kohl, *Synth. Methods Organomet. Inorg. Chem.*, 2000, **9**, 178.

[14] E. O. Fischer, *Rev. Pure Appl. Chem.*, 1974, **24**, 407.

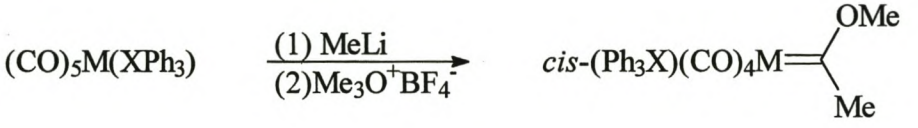
[15] E. O. Fischer and R. Aumann, *Angew. Chem. Int. Ed. Engl.*, 1967, **6**, 879.

[16] E. O. Fischer and R. Aumann, *Chem. Ber.*, 1969, **102**, 1495.

[17] C. P. Casey, C. R. Cyr and R. A. Boggs, *Syn. Inorg. Met-Org. Chem.*, 1973, **3**, 249.



Scheme 1.1



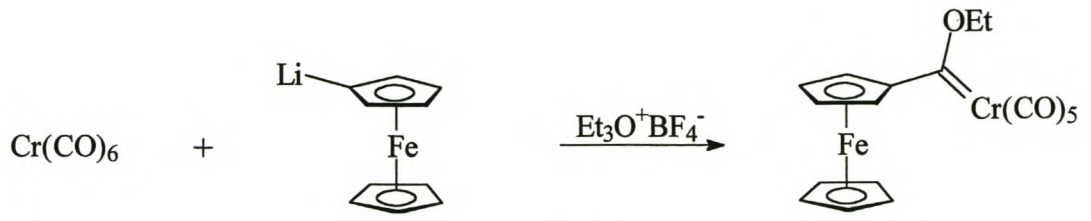
M = Cr, Mo, W

X = P, As, Sb

Scheme 1.2

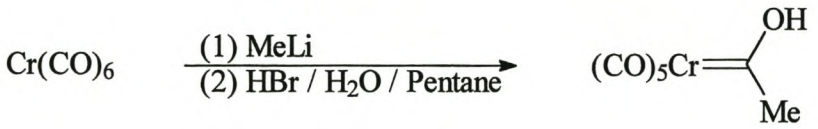
Although Gignard reagents can also be used as alkylating agents, alkyl- and aryl lithium reagents are much more useful nucleophiles to add to metal carbonyls.[18] Even reagents such as ferrocenyllithium can be used (Scheme 1.3).[19]

[18] D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 1971, **5**, 247.
[19] (a) G. A. Moser, E. O. Fischer and M. D. Rausch, *J. Organomet. Chem.*, 1971, **27**, 379. (b) J. A. Connor, E. M. Jones and J. P. Lloyd, *J. Organomet. Chem.*, 1970, **24**, C20.



Scheme 1.3

The first hydroxycarbene complexes for group 6 metals were isolated in 1973 (Scheme 1.4).[20]



Scheme 1.4

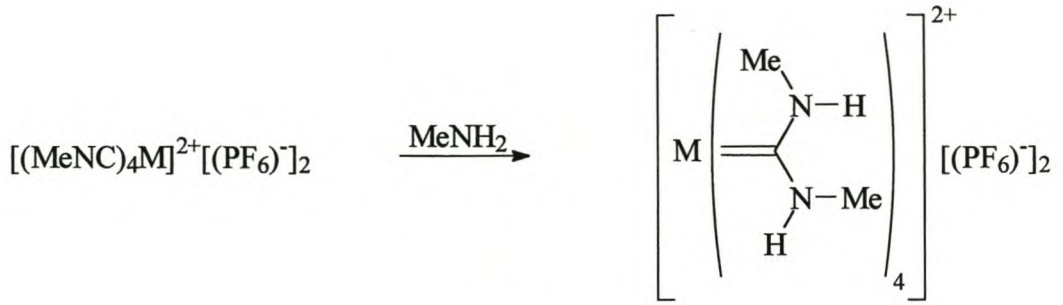
Fischer *et al.* also synthesised the first dihetero-atomic carbene complexes (Scheme 1.5).[21]

Scheme 1.5

The nucleophilic addition of alcohols and amines to isonitriles of chromium also yield dihetero-atomic carbene complexes,[22] whereas the isonitriles of molybdenum and

[20] E. O. Fischer, G. Kreis and F. R. Kreissl, *J. Organomet. Chem.*, 1973, **56**, C37.
[21] E. O. Fischer and H.-J. Kollmeier, *Angew. Chem. Int. Ed. Engl.*, 1970, **9**, 309.
[22] (a) D. F. Christian, G. R. Clark and W. R. Roper, *J. Organomet. Chem.*, 1974, **81**, C7. (b) E. M. Bradley, J. Chatt and R. L. Richards, *J. Chem. Soc.*, 1971, 21.

tungsten do not react with these weak proton donors.[23] Percarbene complexes of platinum and palladium prepared in this way are surprisingly stable (Scheme 1.6).[24]



M = Pd, Pt

Scheme 1.6

It is also possible to alkylate neutral acyl complexes in an analogous way to the alkylation of lithium acyl metallates, and it has been done for iron,[25] mercury,[26] platinum[27] and manganese.[28] However, group 6 carbene complexes are only prepared via the anionic intermediate.

Some transition metal complexes react with organic salts or salt-like reagents to afford a wide variety of carbene complexes (Schemes 1.7 and 1.8).[29]

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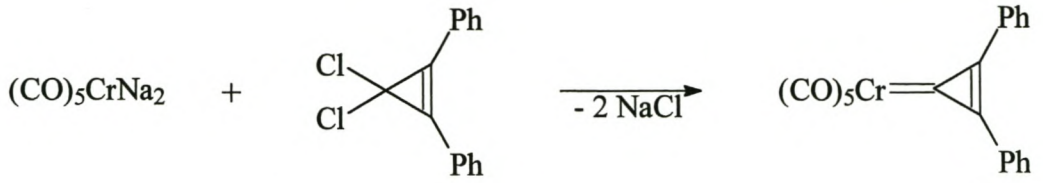
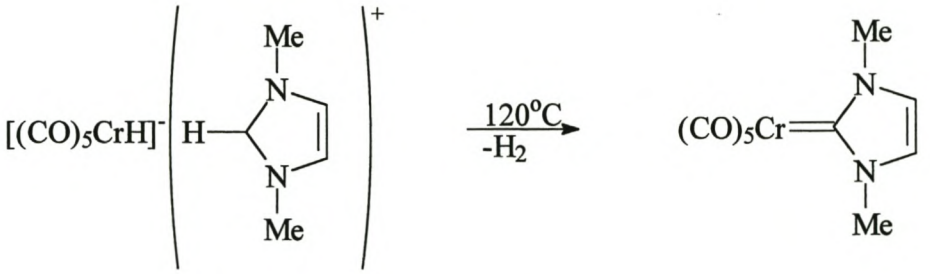
[23] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd and J. A. McCleverly, *J. Chem. Soc. Dalton Trans.*, 1972, 1246.
[24] J. S. Miller and A. L. Balch, *Inorg. Chem.*, 1972, **11**, 2069.
[25] H. Felkin, B. Meunier, L. Pascord and J. Prange, *J. Organomet. Chem.*, 1977, **135**, 361.
[26] U. Schöllkopf and F. Gerhart, *Angew. Chem. Int. End. Engl.*, 1967, **6**, 560.
[27] E. D. Dobrzynski and R. J. Angelici, *Inorg. Chem.*, 1975, **14**, 1573.
[28] C. H. Gume, M. Green, J. R. Moss and F. G. A. Stone, *J. Chem. Soc. Dalton. Trans.*, 1974, 351.
[29] (a) K. Öfele, *Angew. Chem. Int. Ed. Engl.*, 1968, **7**, 950. (b) K. Öfele, *J. Organomet. Chem.*, 1968, **12**, P42.

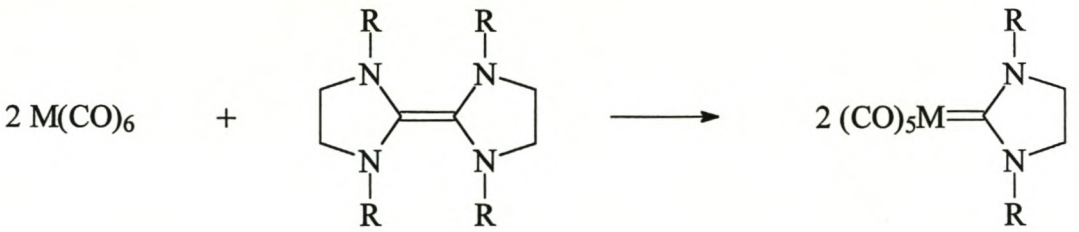


Scheme 1.7



Scheme 1.8

Stable metal carbene complexes can be obtained form electron-rich olefins with weak carbon-carbon double bonds that exhibit nucleophilic character and metal complexes susceptible to nucleophilic attack (Scheme 1.9).[30]



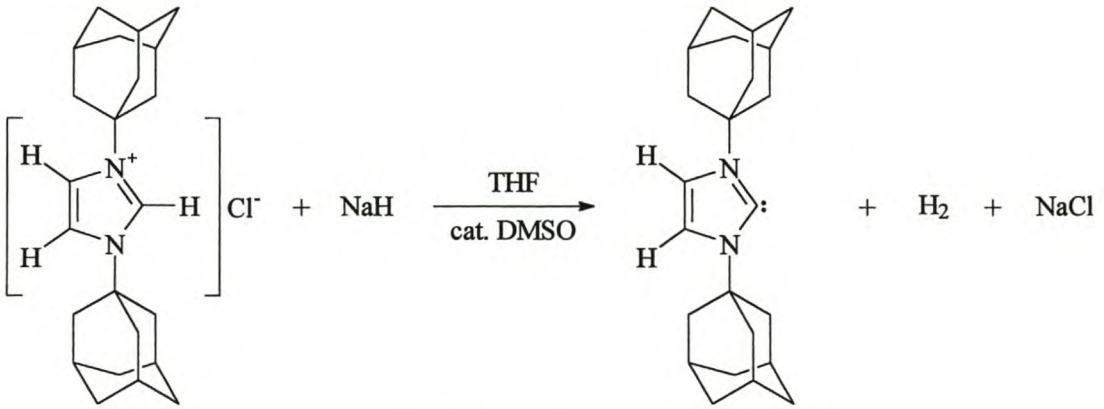
R = Me, Et, CH_2Ph

M = Cr, Mo

Scheme 1.9

[30] M. F. Lappert and P. L. Pye, *J. Less Common Met.*, 1977, **54**, 191; *Chem. Abstr.*, 1977, **87**, 201, 682U.

Metal carbene complexes can be prepared by using free organic carbenes. In 1991 Arduengo III, *et al.*[31] isolated the first crystalline carbene, 1,3-di-1-adamantylimidazol-2-inilidene (Scheme 1.10), and fully characterized it. The carbene is stable in the absence of air and moisture and only melts at 240 – 241°C.



Scheme 1.10

Initially, it was thought that this carbene is stabilized electronically as well as sterically, but the subsequent preparation of 1,3-dimethylthiazol-2-inilidene showed that steric effects do not play an important role in the stability if these compounds.[32] Since then, many theoretical and physical investigations have shown that the unusual stability of these compounds cannot be ascribed to the cyclic π-delocalization or resonance in the unsaturated imidazole ring only.[33] This was proved when saturated imidazolinidenes were prepared in 1995.[34] Boehme and Frenking[35] found that both the saturated and the unsaturated carbenes are stabilized by electron donation from the

[31] A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.
[32] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.
[33] (a) A. J. Arduengo III, D. A. Dixon, K. K. Kumashiro, C. Lee, W. P. Power and K. W. Zilm, *J. Am. Chem. Soc.*, 1994, **116**, 6361. (b) A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6812. (c) A. J. Arduengo III, H. V. R. Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster and T. F. Koetzle, *J. Am. Chem. Soc.*, 1994, **116**, 6812.
[34] A. J. Arduengo, J. R. Goerlich and W. J. Marshall, *J. Am. Chem. Soc.*, 1995, **117**, 11027.
[35] C. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1995, **118**, 2039.

lone pairs on the nitrogen atom to the formally empty $p_\pi(C_2)$-orbital. The unsaturated carbenes are slightly more stable than their saturated counterparts, due to the π-delocalisation in the pseudo-aromatic ring. This causes a significant electronic charge in the p_π-orbital of the carbene carbon and a resulting decrease in the electrophilicity of the carbene. However, additional steric protection of the carbene carbon can be used to compensate for the somewhat lower electronic stabilisation that is calculated for saturated imidazolidinilenes.

The introduction of these Arduengo-type free carbenes sparked renewed interest in heterocylic transition metal carbene complexes. Imidazolidinilene complexes of chromium,[36] tungsten,[37] iron[34(a)] and zinc,[38] have been synthesized and characterized, as well as homoleptic complexes of nickel,[39] platinum,[40] copper and silver.[41] These new complexes may be more effective than more traditional phosphine complexes in homogeneous catalysis,[42] especially because the imidazolinylidene ligand does not dissociate as easily as the phosphine ligand. This makes these imidazolinylidene complexes ideally suited as catalysts for asymmetric reactions such as hydrogenation and isomerism.[43]

The use of alkyl iodides instead of alkyloxonium salts as alkylating reagents is a very useful alternative in preparing carbene complexes with a greater variety of alkyl moieties. Other advantages include the fact that alkyl iodides are generally cheaper and

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[36] (a) K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Hertwick, W. Scherer and J. Mink, *J. Organomet. Chem.*, 1993, **459**, 177. (b) N. Kuhn, T. Kratz, R. Boese and D. Bläser, *J. Organomet Chem.*, 1994, **470**, C8.

[37] W. A. Herrmann, L. J. Goossen, G. R. J. Artus and C. Köcher, *Organometallics*, 1997, **16**, 2472.

[38] A. J. Arduengo III, H. V. R. Dias, F. Davidson and R. L. Harlow, *J. Organomet. Chem.*, 1993, **462**, 13.

[39] W. A. Herrmann, G. Gerstberger and M. Spiegler, *Organometallics*, 1997, **16**, 2209.

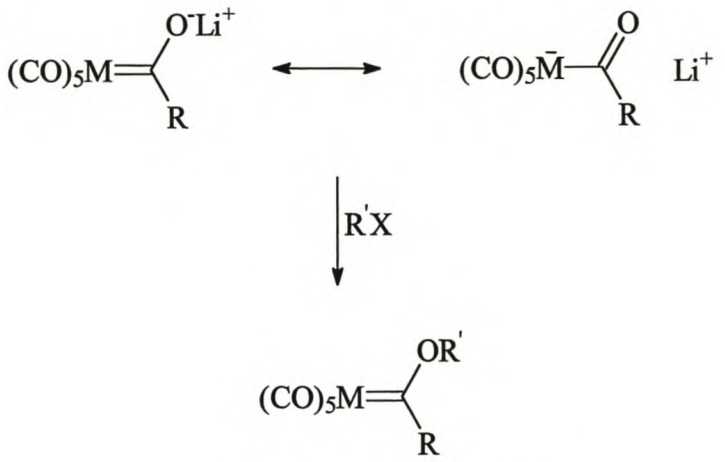
[40] A. J. Arduengo III, S. F. Gamper, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, 1994, **116**, 4391.

[41] A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese, and F. Davidson, *J. Am. Chem. Soc.*, 1993, **12**, 3405.

[42] W. A. Herrmann, L. J. Goossen, M Spiegler, *Organometallics*, 1998, **17**, 2162

[43] W. A. Herrman and C Kocher, *Angew. Chem. Int Ed. Engl.*, 1997, **36**, 2162

less toxic than their methoxy counterparts and it enables chemists to perform a one-pot synthesis in preparing carbene complexes. Methyl, primary, secondary and tertiary alkyl iodides work well (Scheme 1.11).[44]



R = Me, *n*-Bu, Ph, HC=C(Me)$_2$

R' = A wide variety of alkyl substituents

Scheme 1.11

(iii) Structure

The carbene carbon, metal atom, X and Y (see Figure 1.2) are co-planar, the bond lengths showing the sp^2-character of C_{carb}. The M-CO bonds are shorter than the M-C_{carb} bond because the π-acceptor/σ-donor ratio is significantly lower for carbene ligand than for CO. This is true especially of the M-CO bond for the carbonyl ligand *trans* to the carbene ligand, which is even shorter than the *cis*-CO-M bonds. The back donation from M to CO is enhanced by the presence of the *trans*-carbene group – an uneven competition for the non-bonding electrons localised on M exists.[45]

[44] T. R. Hoye, K. Chen and J. R. Vyvyan, *Organometallics*, 1993, **12**, 2806.
[45] P. E. Baikie, E. O. Fischer and O. S. Mills, *Chem. Commun.*, 1967, 1199.

The cause for these discrepancies in bond length lies in the high electrophilicity of the carbene carbon. The high electrophilicity leads to multiple bonding of the carbene carbon atom with the heteroatom, resulting in substantially less back bonding to the metal atom. The C_{carb} p_z-orbital interacts more strongly with the filled p_z-orbitals of the heteroatoms than with the higher energy d-orbitals of the metal. Therefore the C_{carb}-atom acts as a very strong σ-donor, but is a weak π-acceptor, comparable to a tertiary phosphine. There are three possible resonance structures if X is a hetero-atom (Figure 1.2); four if Y is a heteroatom too, and only two if neither X nor Y is a heteroatom.

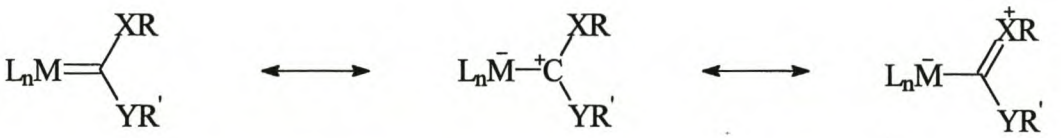


Figure 1.2: *Resonance structures of the metal carbene complex if YR' does not have lone pairs*

The lack of stabilizing resonance explains the relative lability of non-hetero-atom stabilised carbene complexes. NMR studies also confirm the very low rotational barrier around the M-C_{carb} bond unless steric crowding plays a role.[13(b)]

Nakatsuji *et al.*[46] did MO calculations using the *ab initio* SCF method to determine the strength and nature of the M-C_{carb} bond in the model compound $(CO)_5Cr[C(OH)H]$ in order to explain the reactivity of Fischer-type carbene complexes. They have found that the rotational barrier around the M-C_{carb} bond (fixed at

[46] H. Nakatsuji, J. Ushio, S. Han and T. Yonesawa, *J. Am. Chem. Soc.*, 1983, **105**, 426.

2.04 Å) is 0.41 kcal/mol. The corresponding values for ethylene[47] and ethane[48] are 65 kcal/mol and 2.9 kcal/mol, respectively.

The large chemical shifts of carbene carbons generally lead to the belief that C_{carb} is very positively charged. However, this has not been borne out by MO calculations, which have shown that the charge on a carbene carbon is actually a negative one – at around -0.2.[46] The carbonyl carbons are slightly positively charged. This leads to the conclusion that nucleophilic attacks on the carbene carbon are not charge controlled but frontier orbital controlled.[49]

The primary feature of a nucleophilic reaction is that it is governed by the LUMO of the reactant. The site of the reaction is at the AO whose coefficient is the largest in the LUMO. The p_{π}-AO of C_{carb} has the largest coefficient, and this explains why the carbene carbon is the site for nucleophilic attack.[44]

(iv) Reactions of carbene complexes

Metal carbene complexes are the organometallic counterparts of organic esters and are much more reactive. One of the most important reactions that carbene complexes undergo is aminolysis – substitution of the methoxy substituent by a primary or secondary amine (Scheme 1.12).[50] The mechanism of this reaction will be explained in Chapter 2, which deals with aminocarbene complexes. Tertiary amines replace the carbene ligand.[51]

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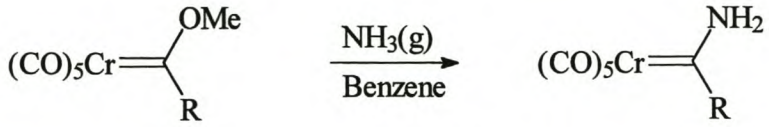
[47] J. E. Douglas , B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, 1955, **23**, 315.
[48] J. P. Lowe, *Prog. Phys. Org. Chem.*, 1968, **6**, 1.
[49] (a) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, 1952, **20**, 722. (b) T. F. Black, R. F. Fenske and C. P. Casey, *J. Am. Chem. Soc.*, 1976, **98**, 441. (c) W. B. Perry, T. F. Schaaf, W. L. Jolly, L. J. Todd and D. L. Cronin, *Inorg. Chem.*, 1974, **13**, 2038.
[50] U. Klabunde and E. O. Fischer, *J. Am. Chem. Soc.*, 1967, **89**, 7141.
[51] E. O Fischer, B. Heckl and H. Werner, *J. Organomet. Chem.*, 1971, **28**, 359.

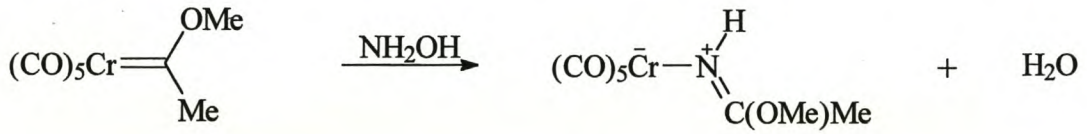


Scheme 1.12

Thiols react with carbene complexes in a similar way to amines (Scheme 1.13).[52]

Scheme 1.13

Carbene complexes also undergo substitution reactions with oximes[53] and hydrazones,[54] as well as an insertion reaction with hydroxylamine. Both *cis*- and *trans*-products form and the ratio of formation is temperature dependent (Scheme 1.14).[54(b)]



Scheme 1.14

Reactions occur which utilise the enhanced acidity of the α-hydrogen atoms of the carbene substituents (Scheme 1.15).[55] This will be discussed in more detail in Chapter 2 with regards to aminocarbenes complexes.

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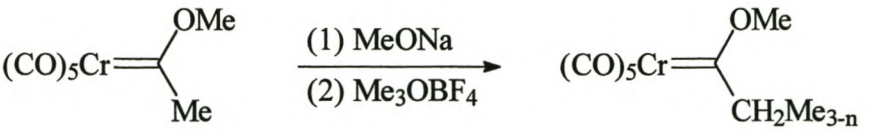
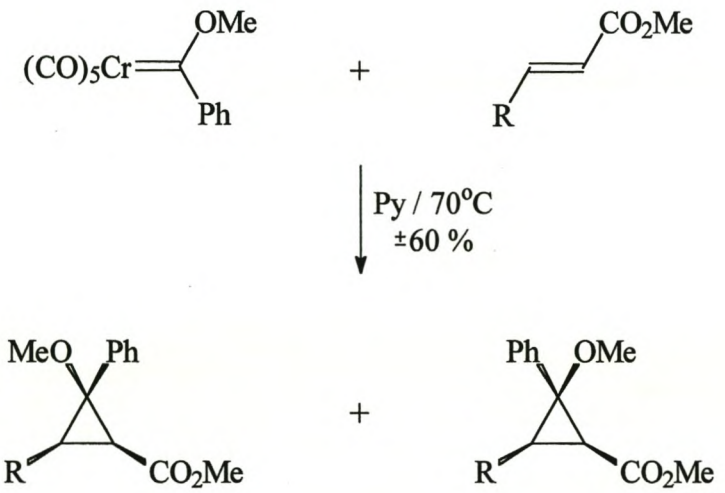
[52] E. O. Fischer, M. Leupold, C. G. Kreiter and J. Muller, *Chem. Ber.*, 1972, **105**, 150.
[53] L. Knauss and E. O. Fischer, *Chem. Ber.*, 1970, **103**, 1262, 3744.
[54] (a) Y. Ito, T. Hirao, and T. Saegusa, *J. Organomet. Chem.*, 1977, **131**, 121. (b) E. O. Fischer and R. Aumann, *Chem. Ber.*, 1968, **101**, 963.
[55] (a) E. O. Fischer, *Proc. Int. Conf. Coord. Chem.*, 11th Ed., 1968, **E7**, 353. (b) C. G. Kreiter, *Angew. Chem. Int. Ed. Engl.*, 1968, **7**, 390.



Scheme 1.15

Carbene complexes are used in cyclopropanation reactions. The carbene is decomposed thermally or with pyridine in the presence of electron deficient α-β-unsaturated esters (Scheme 1.16).



R	*trans*	*cis*
Me	2.5	1
Ph	3.9	1

Scheme 1.16

Another reaction in which carbene complexes are used frequently is benzannulation. Chromium is the metal template of choice in this reaction due to its excellent chemo- and regioselectivity under mild conditions. Other transition metals such as molybde-

num, tungsten and manganese are also used, but they require harsher reaction conditions and are not as selective.[56] Natural products containing a complex structure of fused benzene rings have been prepared using metal carbene complexes. An example is fredericamycin A, an anti-tumour antibiotic (Figure 1.3),[57] which has been made by the reaction of an oxygenated aryl chromium carbene complex with a highly functionalised internal alkyne which, in its turn, originates from a tungsten carbene complex.[58]

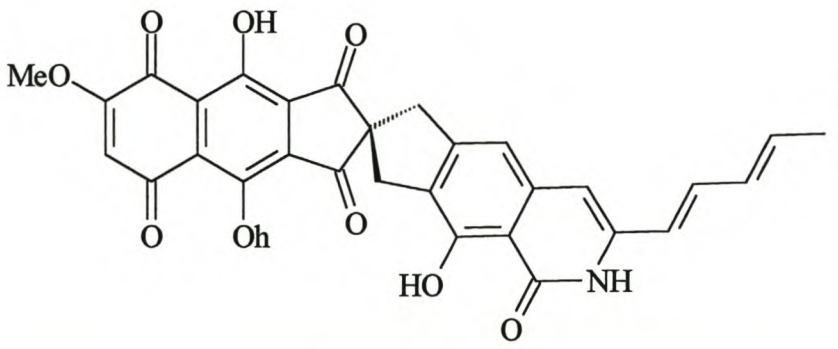


Figure 1.3: *Fredericamycin A*

Formal cyclo-addition of alkynes to a α-β-unsaturated carbene complex with carbonyl insertion, of which the above is an example, is known as the Dötz reaction[59] and is capable of yielding a host of organic products such as hydroquinone monoethers[60] and cyclohexadienones.[61]

[56] K. H. Dötz and P. Tomuschat, *Chem. Soc. Rev.*, 1999, **28**, 187.
[57] D. L. Boger O. Hüter, K. Mbiya and M. Zhang, *J. Am. Chem. Soc.*, 1995, **117**, 11839.
[58] J. Bao, W. D. Wulff, V. Dragisich, S. Wenglowsky and R. G. Ball, *J. Am. Chem. Soc.*, 1994, **116**, 7616.
[59] A. de Meijere, *Pure Appl. Chem.*, 1996, **68(1)**, 61.
[60] K. H. Dötz, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 587.

1.4 Objectives of this study

It is clear that metal carbene complexes are very useful as starting materials in organic syntheses. They are similar to organic esters, but are more reactive due to the strong electron withdrawing properties of the pentacarbonyl metal moiety.[62] Different uses of metal carbene complexes in organic synthesis are summarized in Figure 1.4.[63]

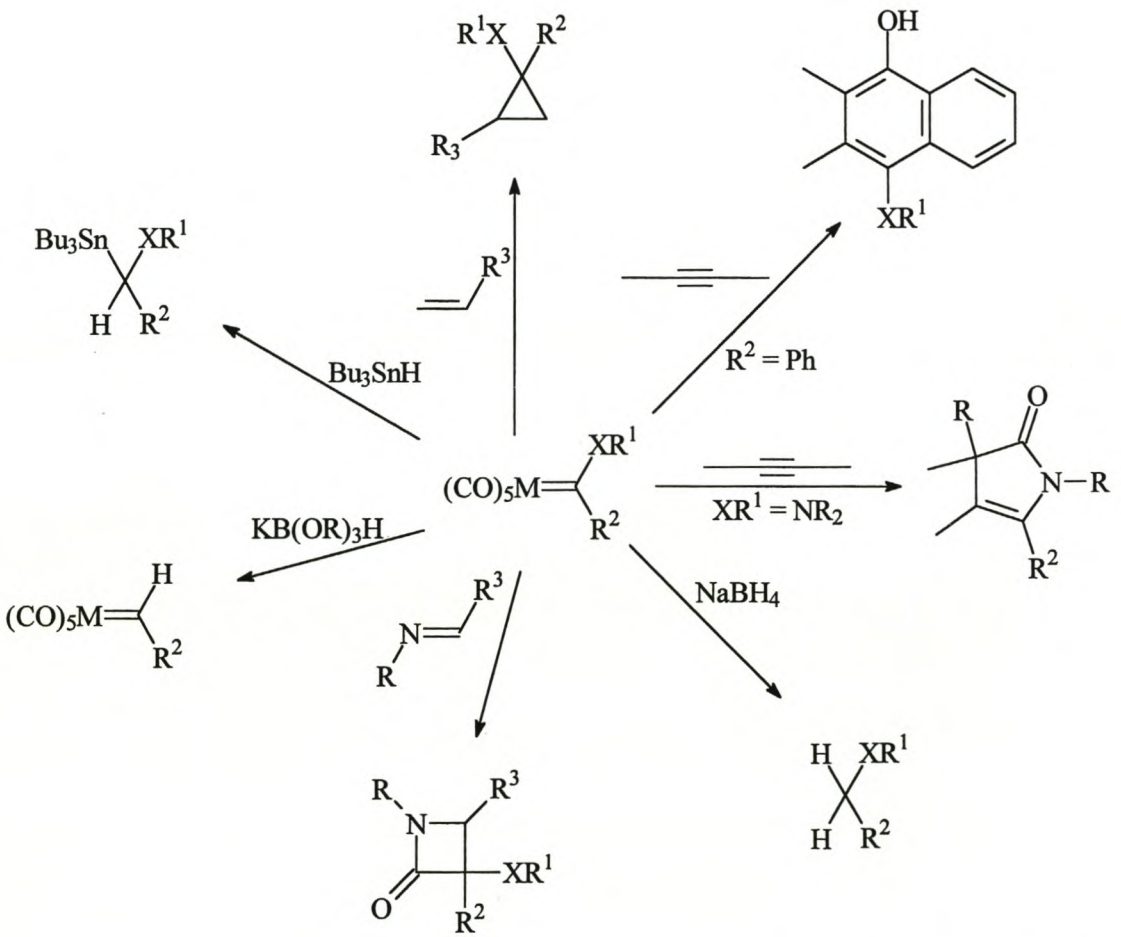


Figure 1.4: *Synopsis of synthetic possibilities utilising metal carbene complexes*

[61] P. C. Tang and W. D. Wulff, *J. Am. Chem. Soc.*, 1984, **106**, 1132.
[62] K. Fuchibe and N. Iwasawa, *Tetrahedron*, 2000, **56**, 4907.
[63] H. Rudler, A. Parlier, T. Durand-Réville, B. Martin-Vaca, M. Audouin, E. Garrier, V. Certal and J. Vaisserman, *Tetrahedron*, 2000, **56**, 5001.

Some of these reactions will be referred to in Chapters 2 and 3. The important thing to notice, however, is that the substituents on the carbene carbon are incorporated in the structure of the final product in most of these reactions. Therefore, if metal carbene complexes can be synthesized that have novel substituents on the carbene carbon, they can be used as precursors in organic synthesis.

The aim of the present study was, firstly, to synthesize carbene complexes of group 6 metals utilizing 2-amino-thiazoles as substituents. Given the importance of thiazoles in organic synthesis and living systems, these new complexes might be useful as precursors in synthetic organic chemistry. This will be discussed in more depth in Chapter 2 of this study, together with an overview of the literature on aminocarbene complexes and the results of the study.

The second aim was to prepare bimetallic complexes, containing group 4 and group 6 metals. The reactivity of the carbene moiety is modulated by the presence of the metal-containing ligand. This makes these complexes useful in organic synthesis.[64] The results of this part of the study, together with an overview of the relevant literature, will be presented in Chapter 3.

[64] J. Barluenga and F. J. Fañanás, *Tetrahedron*, 2000, **56**, 4597.

Chapter 2

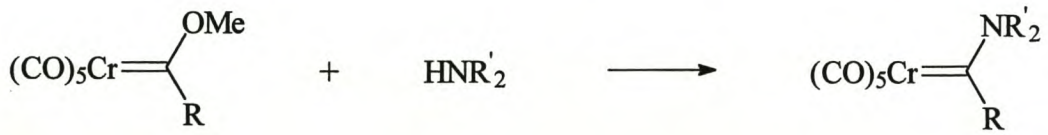
Aminocarbene complexes with thiazolyl ligands

2.1 Introduction

2.1.1 Aminocarbene complexes

(i) Synthesis

Aminocarbene complexes were discovered shortly after the first planned synthesis of an alkoxycarbene complex.[1] The discovery that ammonia, and primary and secondary amines do not replace a carbonyl ligand the way phosphines do, was a surprising one. However, subsequent studies revealed that the bond lengths of alkoxycarbene complexes are similar to the corresponding bond lengths of organic esters.[2] Similar bond lengths imply comparable bond strengths and reactivity and therefore alkoxycarbene complexes can undergo aminolysis similarly to esters. The preparation (Scheme 2.1) is easily performed at low temperatures, the separation is facile and the yield is high.



Scheme 2.1

[1] U. Klabunde and E. O. Fischer, *J. Am. Chem. Soc.*, 1967, **89(26)**, 7141.
[2] K. H. Dötz, T. Schäfer and K. Harms, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 176.

Sterically hindered amines such as diisopropyl amine or dibenzyl amine do not react in this way. However amines such as isoindoline do (Figure 2.1).[3]

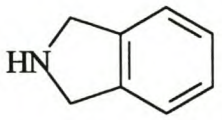


Figure 2.1 *Isoindoline*

At this point, it is necessary to look at the reaction mechanism[4] for aminolysis (Figure 2.2).[5] In the reaction scheme HX is a proton donating species and Y is a proton acceptor. The rate law is given by

$$D[A]/dt = K_n[B][RNH_2][HX][Y].$$

In an inert solvent (such as pentane) the amine must provide both the proton donor and the proton acceptor. The need for a proton donor and a proton acceptor in the reaction mechanism explains the use of an excess amount of amine. It is clear that a sterically hindered amine will react with more difficulty unless a solvent is used that can act as proton donor/acceptor, such as dioxane or furane.

Another curious characteristic of the aminolysis reaction is its negative reaction energy. This can be accounted for by assuming that proton transfer from RNH_2 to Y is immediately after or synchronous with the formation of the carbon-nitrogen bond.[6]

---

[3] A. Hafner, L. S. Hegedus, G. de Weck, B. Hawkins and K. H. Dötz, *J. Am. Chem. Soc.*, 1988, **110**, 8413.
[4] (a) B. Heckl, H. Werner and E. O. Fischer, *Angew. Chem. Int. Ed. Engl.*, 1968, **7**, 817. (b) H. Werner, E. O. Fischer, B. Heckl and C. G. Kreiter, *J. Organomet. Chem.*, 1971, **28**, 367.
[5] D. J. Cardin, B. Çetinkaya and M. F. Lappert, *Chem. Rev.*, 1971, **72(5)**, 565.
[6] H. Werner, E. O. Fischer, B. Heckl and C. G. Kreiter, *J. Organomet. Chem.*, 1971, **28**, 367.

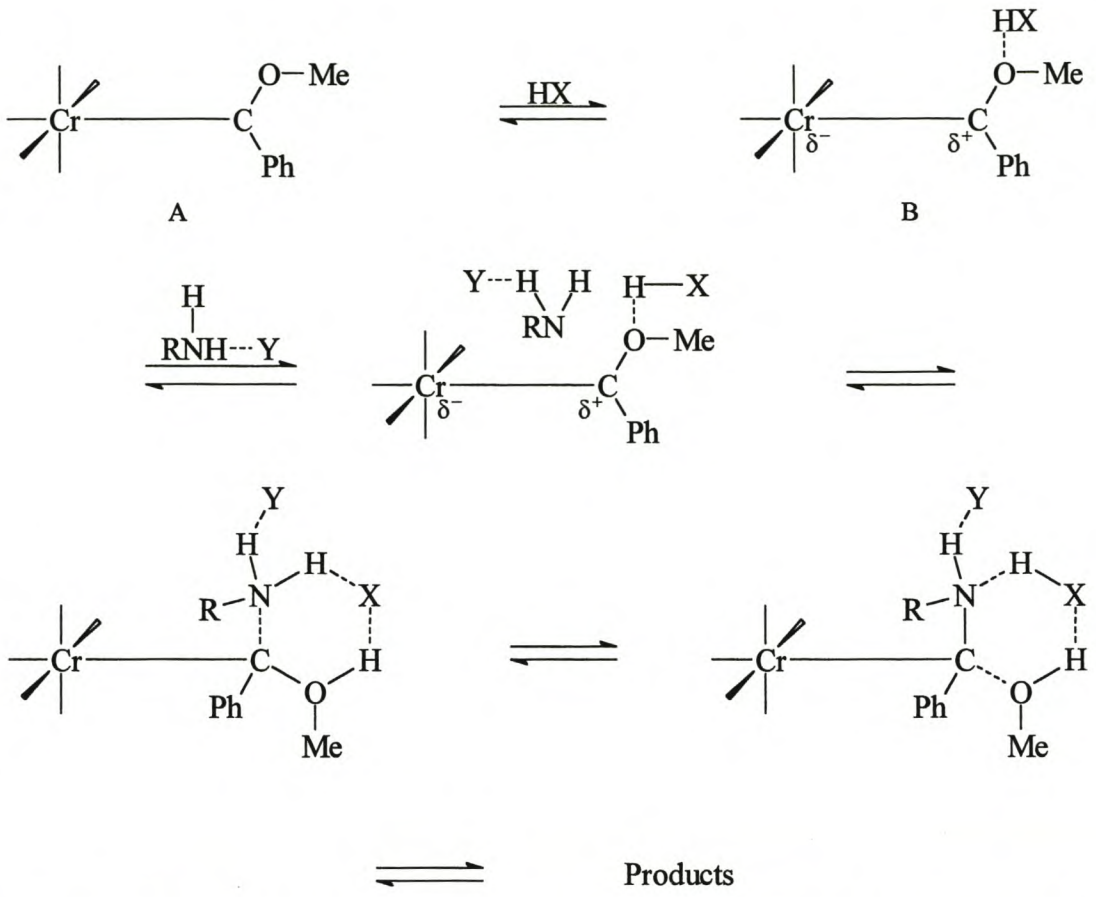
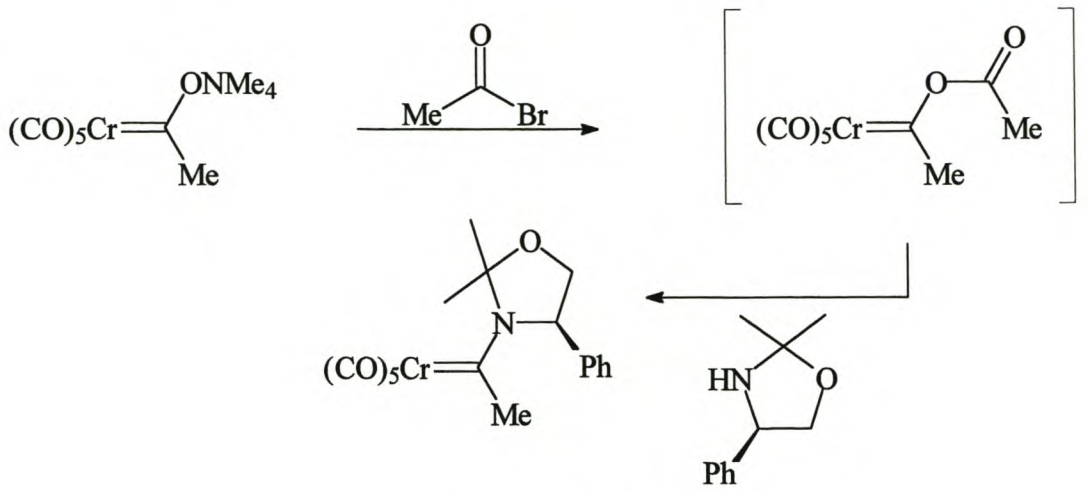


Figure 2.2: *Reaction mechanism for aminolysis. In the figure HX is a proton donor and Y is a proton acceptor.*

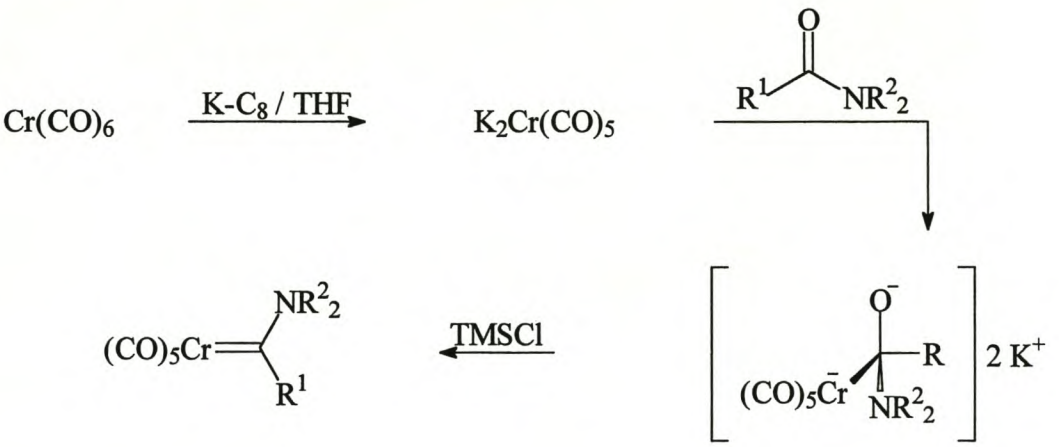
Tertiary amines replace the carbene ligand. In cases where more bulky ligands are used, the use of activated oxy leaving groups can enhance the amine exchange. The (tetramethylammonium)oxy salt undergoes acylation by carboxylic acid halides to yield very reactive oxyacyl carbene complexes (Scheme 2.2).[7] These reactive intermediates are the equivalent of organic mixed anhydrides and react readily with amines to yield aminocarbene complexes.

[7] (a) M. F. Semmelhack and J. J. Bozell, *Tetrahedron Lett.*, 1982, **23**, 2931. (b) L. S. Hegedus, M. A. Schwindt, S. DeLombaert and R. Imwinkelried, *J. Am Chem. Soc.*, 1990, **112**, 2264.



Scheme 2.2

As an alternative route to the Fischer-method of synthesizing aminocarbene complexes, the Hegedus-Semmelhack-method is a way in which a great variety of aminocarbene complexes can be prepared.[8] Chromium hexacarbonyl is reduced by potassium graphite (K-C_8) to produce $K_2Cr(CO)_5$ (Scheme 2.3). This is followed by treatment with alkyl amides, aryl amides or lactames, and finally trimethylsilyl chloride.[9]



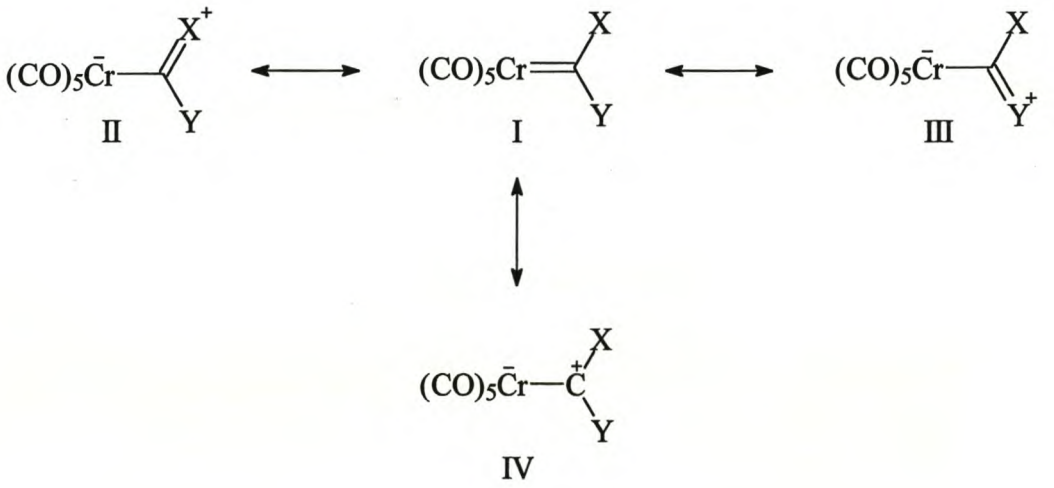
Scheme 2.3

[8] (a) C. Borel, L. S. Hegedus, J. Krebs and Y. Saroh, *J. Am. Chem. Soc.*, 1987, **109**, 1101. (b) R. Imwinkelried and L. S. Hegedus, *Organometallics*, 1988, **7**, 702. (c) M. A. Schwindt, T. Lejon and L. S. Hegedus, *Organometallics*, 1990, **9**, 2814.

[9] M. A. Schwindt, J. R. Miller and L. S. Hegedus, *J. Organomet. Chem.*, 1991, **413**, 143.

(ii) Structure

Replacement of OCH_3 by $N(Et)_2$ causes the M-C_{carb}-bond to lengthen from 2.04 Å to 2.16 Å.[10] This means that the M-C_{carb} bond in an aminocarbene complex has much less double bond character than in an alkoxy carbene complex. In fact the length of the M-C_{bond} in an aminocarbene complex approaches that of a M-C single bond at 2.21 Å.[11] A look at the sp^2-hybridised carbene atom (Scheme 2.4) shows that either the metal or any of the two ligands X and Y might act as potential π-donors, so that four different resonance structures are possible. With X as NR_2, structure II becomes the most important resonance form of the aminocarbene complexes.



Scheme 2.4

The C_{carb}-N bond is about 1.31 Å.[12] This shortening of the bond implies increased double bond character that leads to a higher rotational barrier of approximately 25 kcal/mole for the C_{carb}-N bond.[13] This is a higher rotational barrier than those of the corresponding carboxylic esters and amides, high enough for the rotamers of

[10] J. A. Connor and O. S. Mills, *J. Chem. Soc. A*, 1969, 334.
[11] F. A. Cotton and D. C. Richardson, *Inorg. Chem*, 1996, **1851**, 5.
[12] C. J. Brown, *Acta Crystallogr.*, 1966, **21**, 442.
[13] J. A. Connor and E. O. Fischer, *J. Chem. Soc. (A)*, 1996, **578**.

aminocarbene complexes to be isolable and stable. If the heteroatom becomes a better π-donor, the carbene carbon atom becomes a weaker acceptor of the metal's electron density. Therefore, the metal's back bonding to the carbonyl ligands becomes stronger and this leads to a shortening especially of the *trans*-Cr-CO bond. This effect can be seen in the IR spectra of aminocarbene complexes when compared to those of alkoxycarbene complexes: The infrared absorption of the *trans*-CO group moves to a lower frequency by about 10-20 cm^{-1}.[14] Another way to gather information of the electron density at the metal center is by ^{53}Cr NMR spectroscopy.[15] ^{53}Cr NMR spectroscopy can be used to estimate the efficiency of the π-overlap of the carbene carbon with its substituents and the sensitivity of the π-overlap to steric crowding. A downfield shift relative to $Cr(CO)_6$ is caused by an increase in the steric bulk. This might be because a parallel orientation of the p-orbitals is required for effective π-overlap of the heteroatom with the carbene carbon and steric crowding inhibits this.

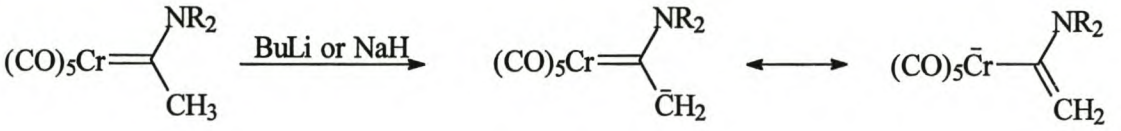
(iii) Reactions and applications in synthetic organic chemistry

Aminocarbene complexes find wide application in organic synthesis[16] and chiral aminocarbene complexes are much more useful than chiral alkoxycarbene complexes.[17] Their utility stems from the fact that their high barrier of rotation around the C_{carb}-N bond gives them one degree of freedom less. This means greater stereoselectivity and so it is possible to synthesize chiral molecules with a good

[14] H. Fischer and F. R. Kreissl; U. Schubert, both in *Transition Metal Carbene Complexes* (D. Seyforth, Ed.), Verlag Chemie, Deerfield Beach, FL, 1983, p69-112.
[15] A. Hafner, L. S. Hegedus, G de Weck, B, Hawkins and K. H. Dötz, *J.Am.Chem. Soc.*, 1998, **110**, 8413.
[16] (a) K. H. Dötz and P. Tomuschat, *Chem. Soc. Rev.*, 1999, **28(3)**, 187. (b) L. S. Hegedus, M. A. Schwindt, S. DeLombaerd, R. Imwinkelried, *J. Am. Chem. Soc.*, 1990, **112**, 2264. (c) D. W. Macomber, P. Madhukar, R. D. Rogers, *Organometallics*, 1989, **8**, 1275.
[17] W. D. Wulff, *Organometallics*, 1998, **17(15)**, 3119.

measure of stereoselectivity.[18] Cyclic amines can also be used, which is another advantage over alkoxycarbene complexes in terms of the variety of substituents and stereoselectivity.[19]

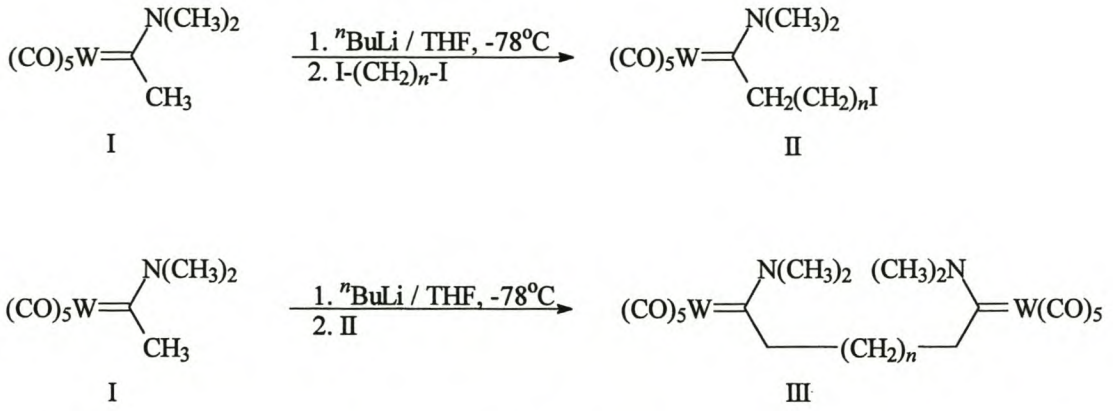
Further functionalization of aminocarbene complexes is possible by deprotonation of N and reaction with electrophiles.[20] Another site for deprotonation is at the carbon atom adjacent to the carbene carbon (if the substituent allows it). This can be done with a strong base such as LDA, BuLi or NaH (Scheme 2.5).



Scheme 2.5

The ambident anion then reacts at the α-carbon atom with alkyl triflate in alkylation reactions,[21] allylic and benzylic bromides[22] or 2-bromocarboxylic esters.[26] In their attemps to synthesize new [μ-bis(carbene)]dimetal complexes, Macomber and Madhukar[23] have found that α-lithio (alkylaminocarbene)-tungsten reacts sequentially with diodoalkanes to yield [μ-bis(carbene)]ditungsten complexes (Scheme 2.6).

[18] K. H. Dötz and R. Weber, *Chem. Ber.*, 1991, **124**, 1635.
[19] L. S Hegedus, R. Imwinkelreid, M. Alarid-Sargent, D. Dvorak and Y. Saton, *J. Am. Chem. Soc.*, 1990, 112, 1109.
[20] D. B. Grotjahn and K. H. Dötz, *Synlett.*, 1991, 381.
[21] M. Adouin, S. Blaudinières, A. Parlier and H. Rudler, *J. Chem. Soc., Chem. Commun.*, 1990, 23.
[22] L. S. Hegedus, M. A. Schwindt, S. De Lombaert and R. Imwinkelried, *J. Am. Chem. Soc.*, 1990, **112**, 2264.
[23] D. W. Macomber and P. Madhukar, *J. Organomet. Chem*, 1992, **433**, 279.



Scheme 2.6

It is possible to functionalize the alkyl substituent on the carbene carbon by adding consecutively buthyllithium, RO_2C-CHO, methanesulfonyl chloride (MsCl) and DBU (1,8-diazabicyclo[5.4.0]undecene-7, Figure 2.3). This affords an α-β-unsaturated ester that can be used in annulation reactions (Scheme 2.7).[24]

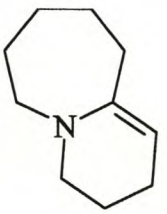
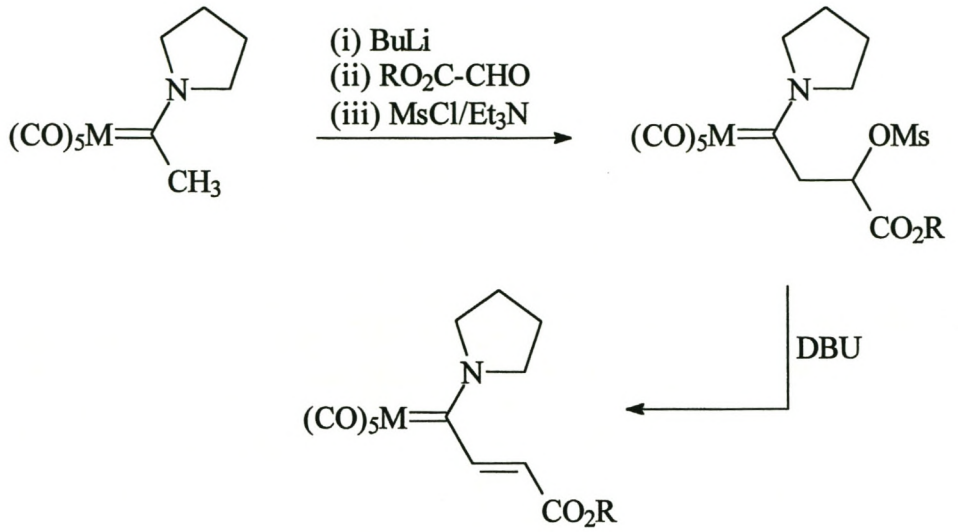


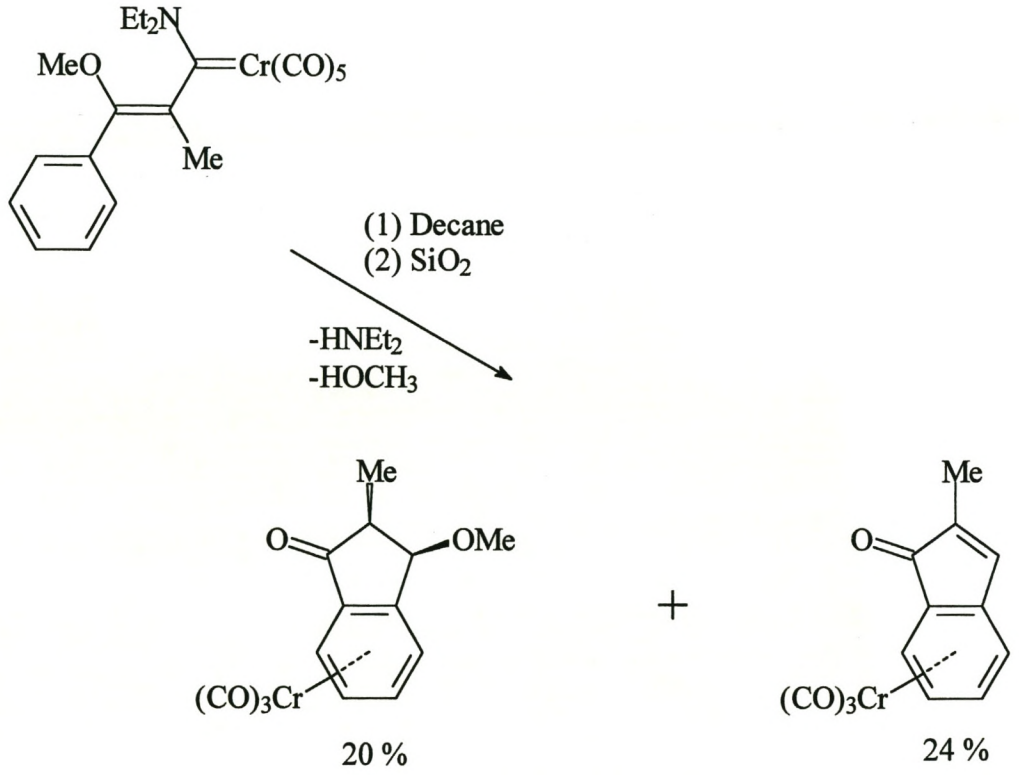
Figure 2.3: *DBU (1,8-diazabicyclo[5.4.0]undecene-7)*

An example of the types of compounds that can be prepared using vinyl carbene complexes is shown in Scheme 2.8 where decane and silicon oxide are added to a chromium carbene complex containing a phenyl group to yield a mixture of ketones.[25]

[24] (a) J. March, *Advanced Organic Chemistry, 5th Ed.*, John Wiley & Sons, New York, 1992. (b) J. Barluenga, L. A. Lopéz, S. Martinéz and M. Tomás, *Tetrahedron*, 2000, **56**, 4967.
[25] K. H. Dötz and I. Pruskil, *Chem. Ber.*, 1978, **111**, 2059.

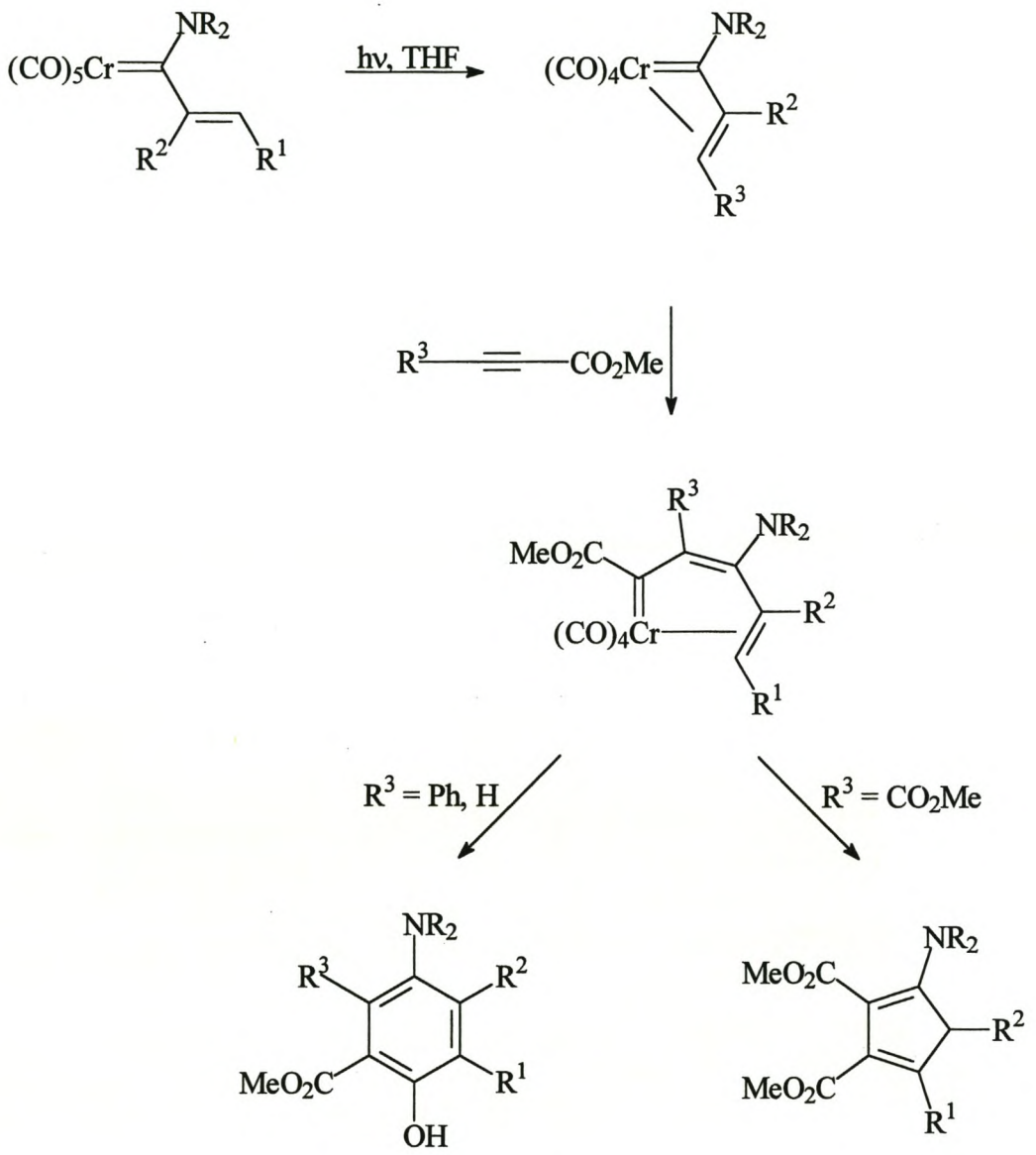


Scheme 2.7



Scheme 2.8

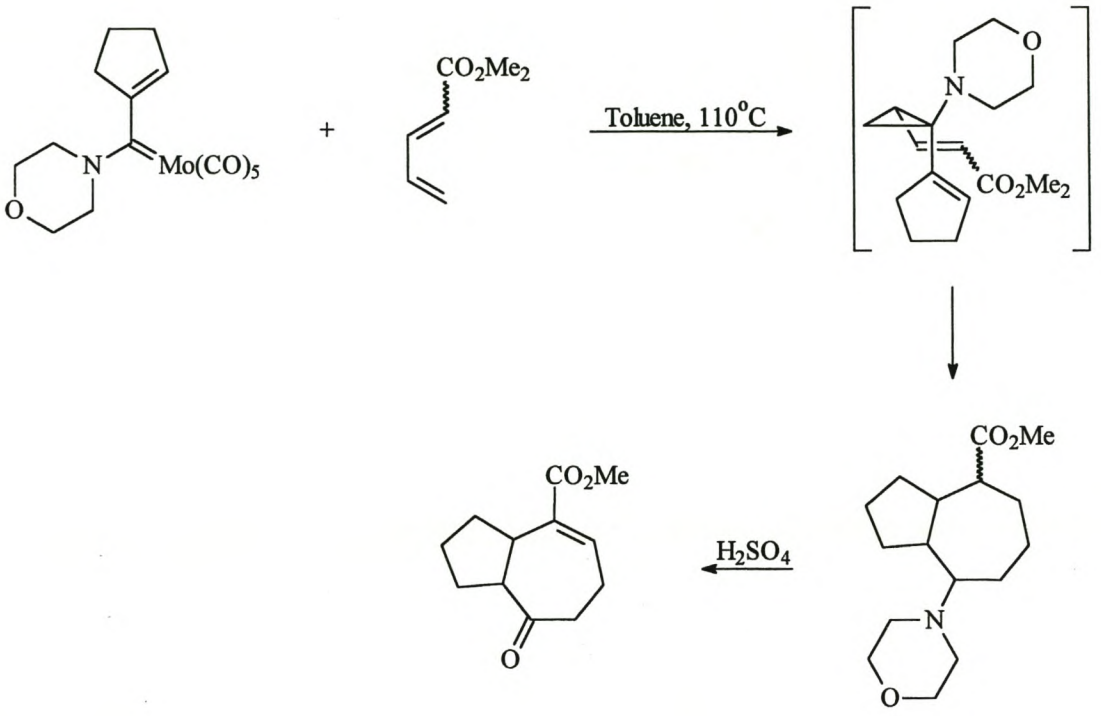
Many other annulation reactions are possible,[26] with high diastereoselectivity[27] including reactions with alkynes to yield substituted benzenes and cyclopentadienes (Scheme 2.9),[28] known as the Dötz reaction.[29]



Scheme 2.9

[26] A. Yamashita, *Tetrahedron Lett.*, 1968, **27**, 5915.
[27] K. H. Dötz, T. Schäfer and K. Harms, *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 176.
[28] (a) M. A. Schwindt, J. R. Miller and L. S. Hegedus, *J. Organomet. Chem.*, 1991, **413**, 143. (b) J. Barluenga, F. Aznar, I. Gutiérrez, A. Martín, S. García-Granda, M. A. Llorca-Baragaño, *J. Am. Chem. Soc.*, 2000, **122**, 1314.
[29] A. de Meijere, *Pure Appl. Chem.*, 1996, **68(1)**, 61.

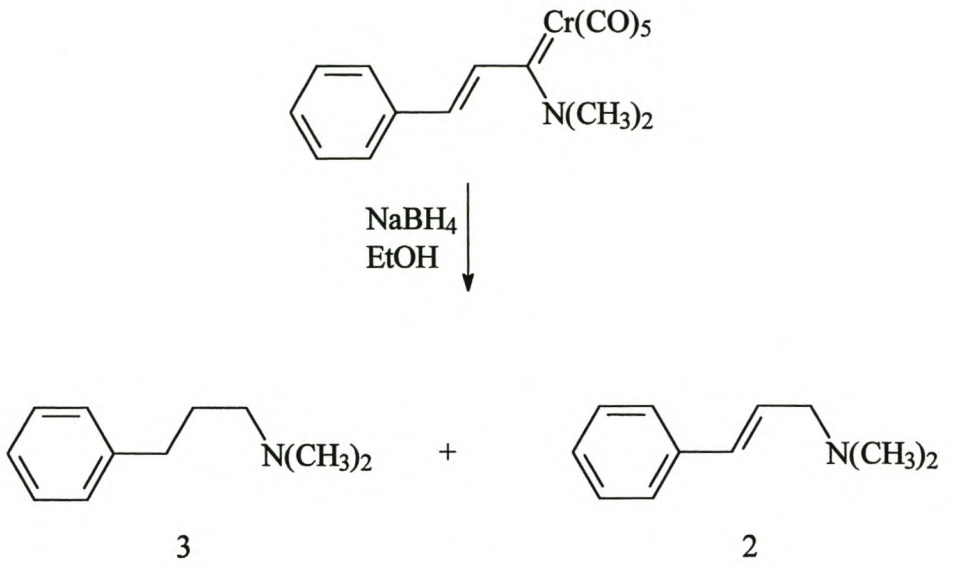
The reaction of an α-β-unsatureted aminocarbene and a diene yields an unstable cyclopropanation product which rearranges to afford a 5-bicyclo[5,3,0]decen-2-one (Scheme 2.10).[30]



Scheme 2.10

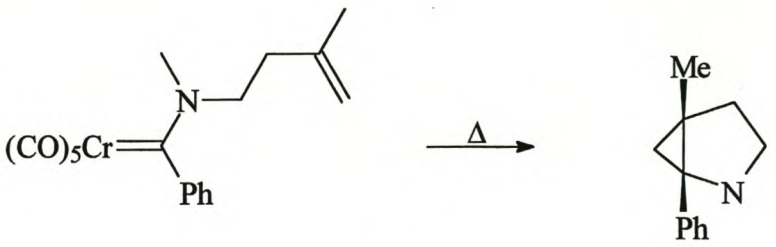
Another synthetic pathway in which aminocarbene compounds are utilized is the complete or partial reduction of α-β-unsaturated aminochromium complexes with $NaBH_4$ (Scheme 2.11).[31]

[30] J. Barluenga, *Pure Appl. Chem.*, 1996, **68(3)**, 543.
[31] M. Gomez-Gallego, M. J. Mancheño, P. Ramirez, C. Piñar and M. A. Sierra, *Tetrahedron*, 2000, **56**, 4893.



Scheme 2.11

Vinylketenes[32] and unsaturated polycyclic lactames can be prepared via hydride and alkyl transfers.[33] The cyclopropanation of electrondeficient olefins using an amino-carbene complex is also a common synthetic route.[34] However, neither alkoxycarbene complexes nor aminocarbene complexes can cyclopropanate an unactivated alkene intermolecularly. The intramolecular reaction, on the other hand, proceeds easily if aminocarbene complexes are used (Scheme 2.12).[35]



Scheme 2.12

[32] L. S. Hegedus and D. B. Miller, Jr., *J. Org. Chem.*, 1989, **54**, 1241.
[33] A. Parlier, R. Yefsah, M. Rudler, J. C Daram and J. Vaissermann, *J. Organomet. Chem.*, 1990, **381**, 191.
[34] T. R. Hoge, G. M Rehberg, *Organometallics*, 1989, **8**, 2070.

2.1.2 The importance of thiazoles

(i) General background.

The thiazoles belong to a large class of organic compounds knows as azoles. Azoles are unsaturated five-membered rings containing two heteroatoms of which one is nitrogen (Figure 2.4).

X		
NH	*Imidazole*	*Pyrazole*
O	*Oxazole*	*Isoxazole*
S	*Thiazole*	*Isothiazole*

Figure 2.4

Although the azoles are classed together, they display a wide variety of chemical behaviour. At the one end of the spectrum oxazoles act similarly to acyclic dienes, to such an extent that electron-rich oxazoles can be used as dienopholes in Diels-Alder reactions.[36] On the other hand, imidazoles act similarly to aromatic systems and display the same reactivity towards electrophilic reagents. Thiazoles fit somewhere in between these two extremes. The organic chemistry of the azoles is varied and many reviews have appeared on the topic.[37] Thiazoles have many uses, among others in anti–cancer[38] and anti–HIV drugs,[39] anti-freeze fluids[40] and dyes.[41]

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[35] (a) B. C Sederberg, L. S. Hegedus, *Organometallics,* 1990, **9**, 313. (b) C. P. Casey, N.L Horming and W.P. Kosner, *J. Am. Chem.Soc.,* 1987, **109**, 4908.
[36] T. L. Gilchrist, *Heterocyclic Chemistry, 2nd Ed.,* Longman, Harlow, 1992, 307.

[37] (a) A. Dondoni and P. Merino, *Comprehensive Heterocyclic Chemistry* (Ed: I. Shinkai), Elsevier, Oxford, 1996, **3**, 373. (b) P. A. Bradley and D. J. Wilkins, *Progr. Heterocyclic. Chem.*, 1997, **9**, 170.
[38] H. I. El-Subbach and A. M. Al-Obaid, *Eur. J. Med. Chem.*, 1996, **31**, 1017.

Thiazole also occurs in nature as a part of the structure of thiamine (Figure 2.5).

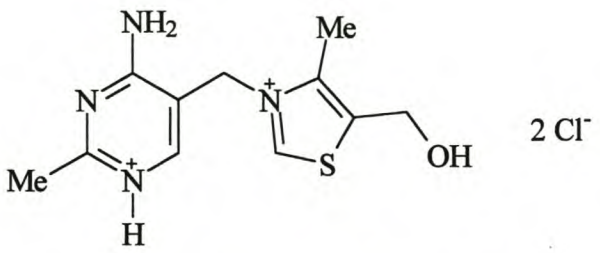

Figure 2.5: *Thiamine (Vitamin B_1)*

Better known as Vitamin B_1, thiamine's most important role occurs during the conversion of carbohydrates to energy.[42] The mechanism by which thiamine catalyzes certain biochemical reactions was investigated by Ronald Breslow who was awarded the Priestley–medal by the American Chemical Society in 1999[43] for this work as well as other contributions to chemistry.

(ii) Thiazoles in organometallic chemistry

Renewed interest has been sparked in the synthesis of transition metal carbene complexes with imidazoles. These new complexes may be more effective than more traditional phosphine complexes in homogeneous catalysis,[44] especially because the imidazolinylidene ligand does not dissociate as easily as the phosphine ligand. This makes these imidazolinylidene complexes ideally suited as catalysts for asymmetric reactions such as hydrogenation and isomerism.[45]

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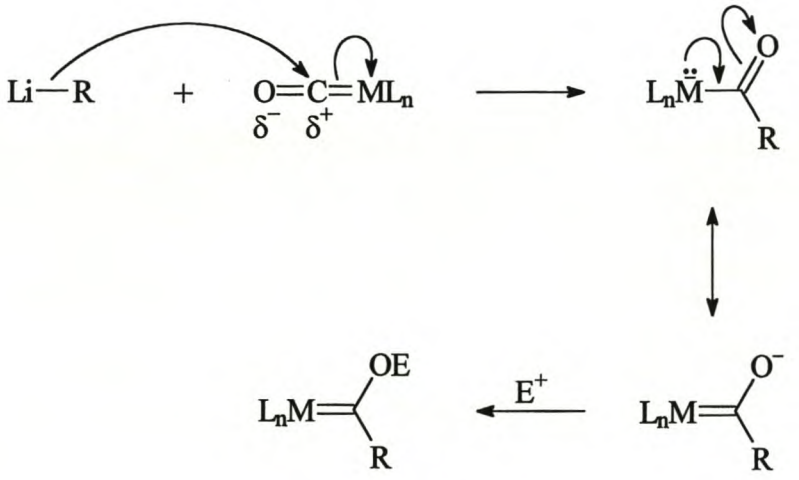
[39] A. Chimirri, S. Grasso, A. Monforte, P. Monforte, A. Rao, M. Zappala, G. Bruno, F. Nicolo and R. Scopelliti, *Farmoco*, 1997, **52**, 673.
[40] H. Watanabe and S. Sugyama, *Antifreezing Fluid Composition*, Jap. Pat 08 085 782, 1996.
[41] S. Beckman, K.-H. Etzbach and S. Ruediger, *Manufacture of Novel Thiazole Methine Dyes*, Ger. Pat DE 4 414 882.
[42] M. van Straaten, *The Healthy Food directory*, New leaf, Dublin, 199, p. 2A.
[43] R. L. Rawls, *Chemical and Engineering News,* March 22 1999, p.33.
[44] W. A. Herrmann, L. J. Goossen, M. Spiegler, *Organometallics*, 1998. **17**, 2162.
[45] W. A. Herrman and C. Kocher, *Angew. Chem. Int. Ed. Engl.*,1997, **36**, 2162.

With this interest in imidazoles, attention has naturally turned towards the thiazoles as well, especially to thiazol-2-yl as ligand. Thiazol-2-yllithium compounds usually are prepared *in situ* by adding buthyllithium to thiazole in ether or THF at –78°C.[46]

The easiest and most useful synthetic route for the preparation of carbene complexes from non-carbene precursors is by the addition of a strong nucleophile such as a carbanion (e.g. thiazolyllithium) to a CO-bond in metal carbonyls - essentially the method employed by Fischer to synthesize the first carbene complexes. The thiazolyllithium ligand's negative change is delocalized to and stabilized by the other π-acceptor ligands (mostly CO) that are coordinated to the metal centre. Alkylation by hard electrophiles (e.g. $R_3O^+BF_4^-$ or $CF_3SO_3CH_3$) yield heteroatom stabilized Fischer-type carbene complexes (Scheme 2.13).[47] The reaction is quick and yield high if a lithium carbanion is used.



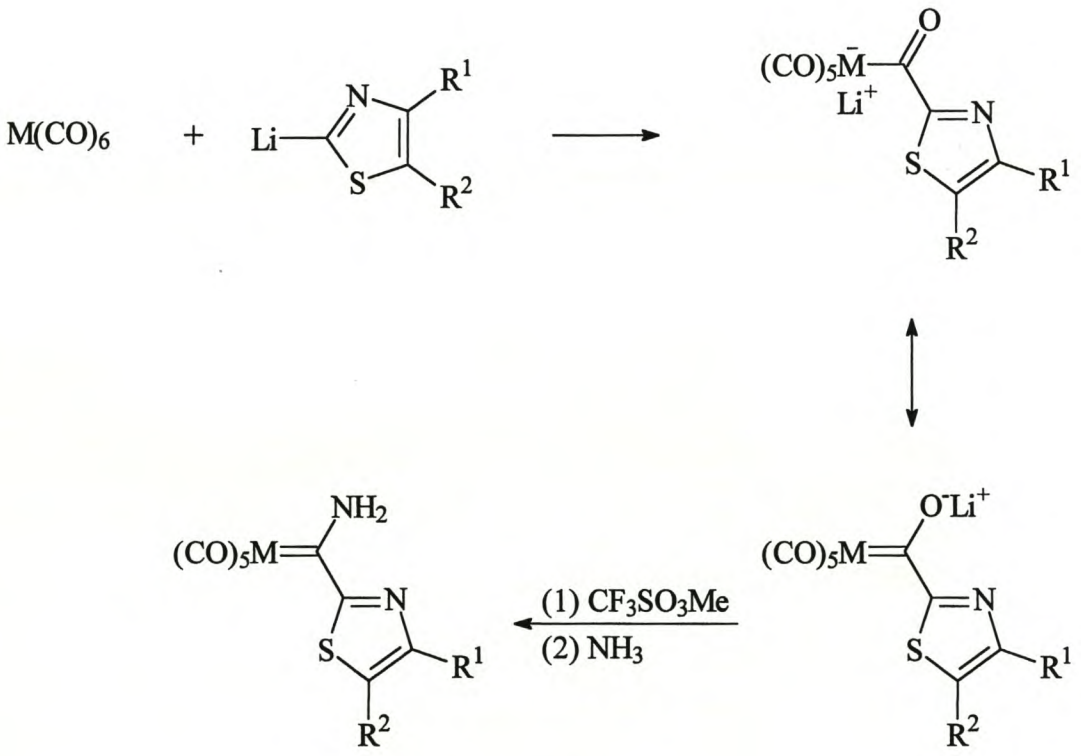
Scheme 2.13

Only a few Fischer-type carbene complexes are known that have been synthesized by the above method of carbonyl functionalization using a thiazolyl group as ligand.

[46] H. Gilman and J. A. Beel, *J. Am. Chem. Soc.*, 1949, **71**, 2328.
[47] K. H. Dötz, *Angew. Chem. Int. Ed. Engl.*, 1984, **23**, 587.

Linford[48] succeeded in preparing [benzothiazol-2-yl(ethoxy)carbene]pentacarbonyl chromium in low yield. Further work in the field has been done by Marais[49] who synthesized compounds containing benzothiazol-2-yl, and Van Niekerk[50] who prepared bimetallic carbene complexes containing benzothiazol-2-yl.

The aim of the present study was to investigate the possibility of preparing Fischer-type aminocarbene complexes that contain a thiazolyl side chain (Scheme 2.14). This type of complex after further deprotonation should be able to function as bidentate ligand and afford binuclear complexes.



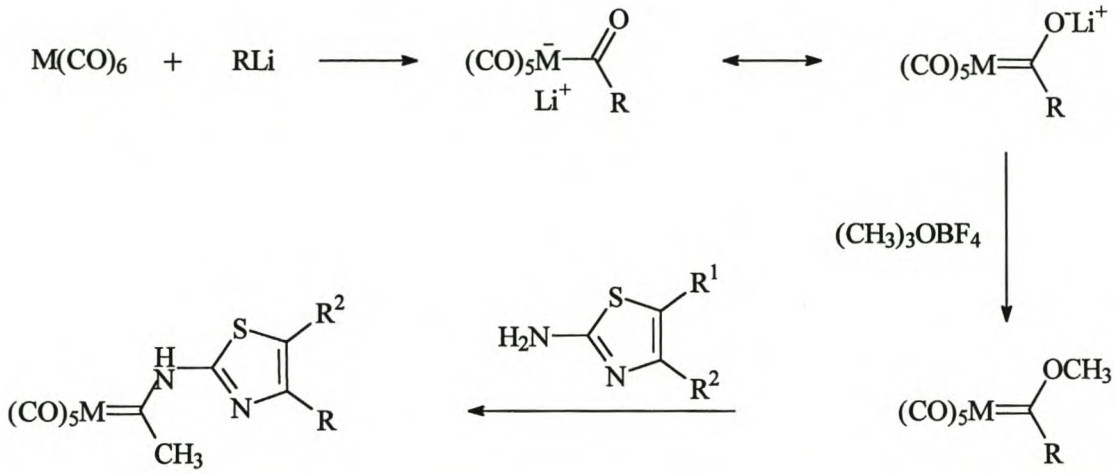
Scheme 2.14

[48] H. G. Raubenheimer, G. J. Kruger, A. van A. Lombard, L. Linford and J.C. Viljoen, *Organometallics*, 1985,**4**, 275.

[49] H. G. Raubenheimer, Y. Stander, E. K. Marais, C. Thompson, G. J. Kruger, S. Cronje and M. Deetlefs, *J. Organomet. Chem.*, 2000, **590**, 148.

[50] L. van Niekerk, *M. Sc .Thesis*, University of Stellenbosch, 1999.

Also, the possibility of preparing aminocarbene complexes that contain a thiazolyl group on the nitrogen atom (Scheme 2.15) was investigated. This type of complex could prove useful in subsequent organic transformations of the Hegedus-type[51] as discussed in the introduction.



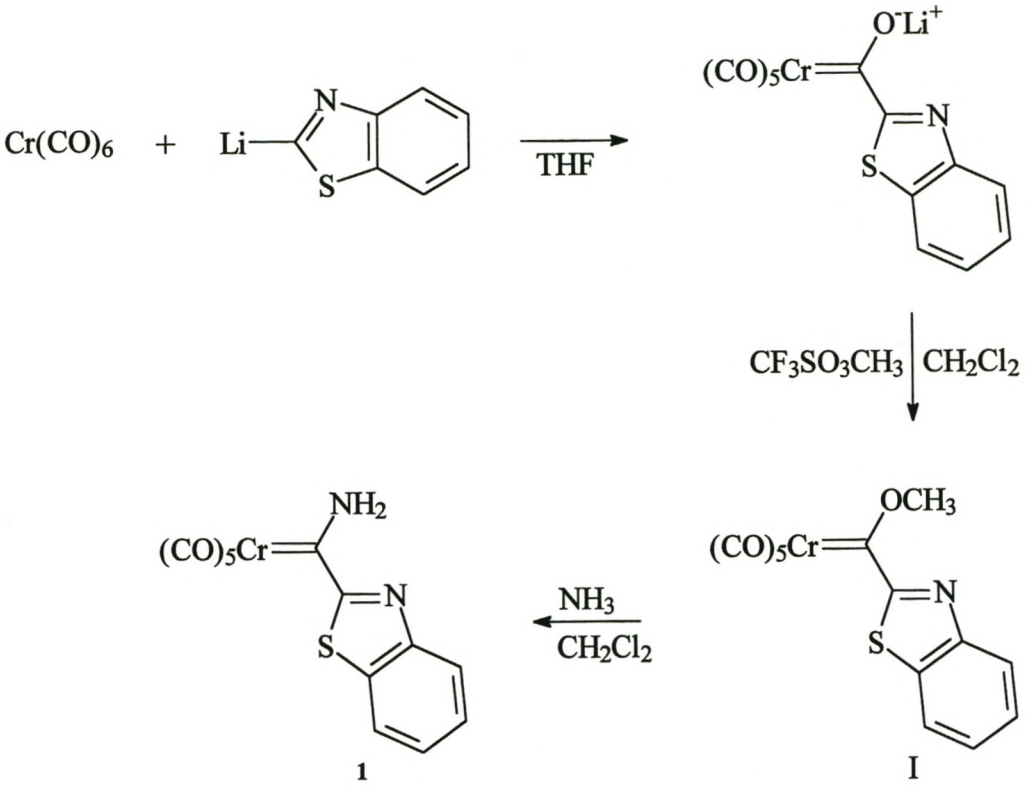
Scheme 2.15

2.2 Results and discussion

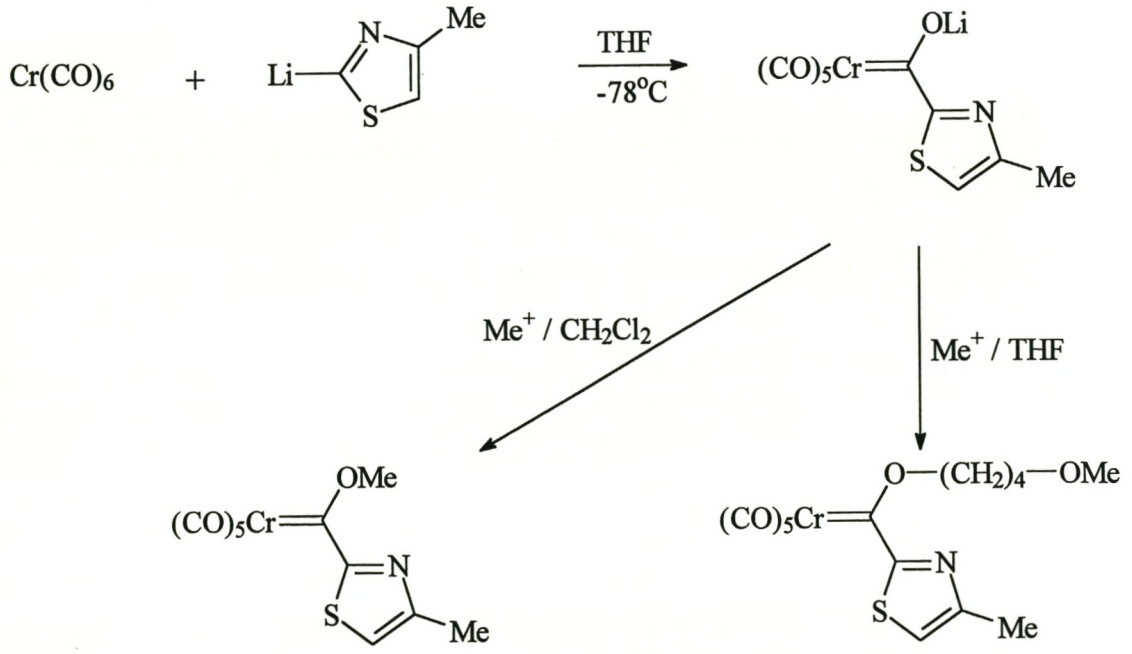
2.2.1 Synthesis of complex (1)

The methoxy precursor to Fischer-type carbene complex **1** was synthesized by reacting benzothiazolyllithium with $Cr(CO)_6$ in THF at –78°C, followed by alkylation with $CF_3SO_3CH_3$ in CH_2Cl_2 (Scheme 2.16). If the alkylation is done in THF, a different product results (Scheme 2.17). The reason for the formation of a different complex in THF is twofold: Firstly, the thiazolyl ligand delocalizes much of the negative charge of the oxygen, and secondly, THF as solvent, is present in large ex-

[51] (a) M. A. Schwindt, J. R. Miller and L. S. Hegedus, *J. Organomet. Chem.*, 1991, **413**, 143. (b) L. S. Hegedus and S D'Andrea, *J. Org. Chem.*, 1988, **110**, 2122. (c) L. S. Hegedus, R. Imwinkelried, M. Alarid-Sargent, D. Dvorak and Y. Satoh, *J. Am. Chem. Soc.*, 1990, **112**, 1109. (d) M. Sierra and L. S. Hegedus, *J. Am. Chem. Soc.*, 1989, **111**, 2335.



Scheme 2.16



Scheme 2.17

cess, both effects leading to initial alkylation of THF, ring opening and alkylation of the anionic carbene complex.[52]

The aminocarbene complex **1** was prepared by bubbling gaseous ammonia through a solution of the neutral precursor complex I in CH_2Cl_2 at 0°C (Scheme 2.16). The product was purified by means of column chromatography at –15°C. Removal of the eluent under vacuum yielded complex **1**. Micro crystals of **1** were obtained by cooling the solution in 1:3 dicloromethane/hexane to –30°C. The complex is soluble in polar organic solvents. In the solid state it is stable in the absence of air and moisture and even seems to remain stable upon prolonged exposure to the atmosphere. Complex **1** is much more stable than its methoxy analogue, due to more π-donation from N to the carbocationic carbon atom.

2.2.2 Spectroscopic characterization of complex 1

(i) NMR spectroscopy

The ^1H and ^{13}C-{^1H} NMR data for complex **1** is summarized in Table 2.1. H^2 of benzothiazole resonates at δ 8.96, and its peak is absent from the ^1H NMR spectrum of **1**. This means that the bonding of the benzothiazole to chromium does indeed occur through C^1. The aromatic protons of benzothiazole move to a slightly lower field in the ^1H NMR spectrum of the carbene complex. There are two peaks for the amino protons. This is indicates that the Cr-C_{carb} bond has much double bond character.

Due to the electron withdrawing effect of the metal-carbene bond, the C_{carb} substituent peaks move to lower field relative to their organic analogues. The occurrence of a peak at very low field, δ 373.1, verifies the presence of the carbene carbon atom in this complex.

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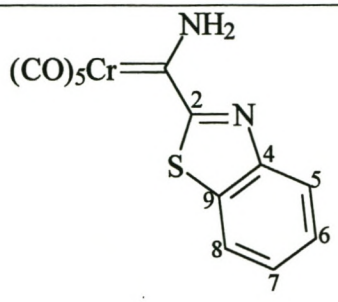
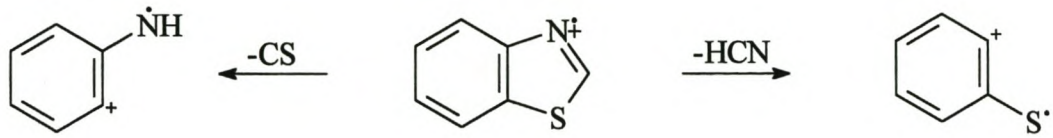
[52] E. K. Marais, *M. Sc. Thesis*, Rand Afrikaans University, 1999.

Table 2.1: *^{1}H and ^{13}C-{^{1}H} NMR data for Complex* ***1***

Complex	
Solvent	$CDCl_3$
H^5	8.17 (1H, m)
$N\underline{H}_2$	10.31 and 8.83 (1H, 2xs)
H^6 and H^7	7.60 (2H, m)
H^8	8.60 (1H, m)
$M=\underline{C}$	373.1
CO_{trans}	222.3
CO_{cis}	216.9
C^2	172.2
C^9	140.0
C^4	151.7
C^5	126.4
C^6	127.8
C^7	127.0
C^8	122.0
C^9	140.0

(ii) Mass Spectroscopy

Free benzothiazole displays two main fragmentation routes upon electron impact (Scheme 2.18).[53] Neutral HCN or CS is expelled to yield one of two possible positively charged free radicals.



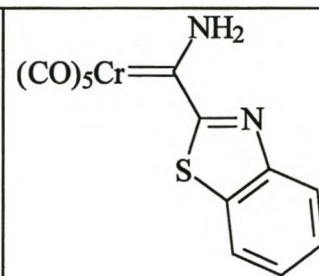
m/z 91 m/z 135 m/z 108

Scheme 2.18

The mass spectroscopic data for complex **1** is shown in Table 2.2.

The molecular ion is very low in intensity. The consecutive loss of the carbonyl ligands, followed by the amino substituent and finally the metal, is evident. The benzothiazole expels HCN, a fragmentation route that is also seen in the free ligand.

Table 2.2: *Mass spectroscopic data for complex 1*

Complex		
m/z	I	Fragment ion
353	1	M^+
325	2	$[M\text{-CO}]^+$

[53]B. J. Millard and A. F. Temple, *Org. Mass Spectrometry*, 1968, **1**, 285.

Table 2.2: *Continued*

297	2	$[M\text{-}2CO]^+$
269	3	$[M\text{-}3CO]^+$
242	6	$[M\text{-}4CO]^+$
214	18	$[M\text{-}5CO]^+$
187	12	$[CrCNC_6H_4S\text{-}o]^+$
135	22	$[CH{=}NC_6H_4S\text{-}o]^+$
108	12	$[C_6H_4S]^+$
52	14	$[Cr]^+$
27	5	[HCN]

(iii) Infrared spectroscopy

The ν(CO) infrared data for carbene complex **1** is summarized in Table 2.3.

Table 2.3: *ν(CO) data for complex 1*

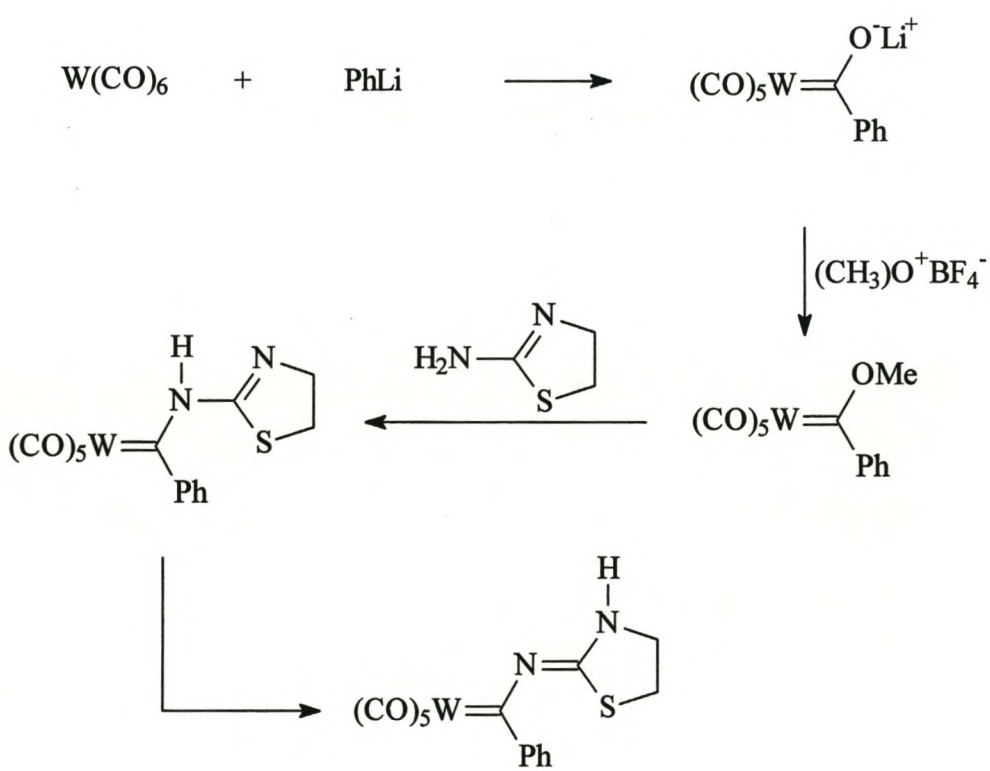
ν(CO)/cm^{-1}		
$A_1^{(1)}$	$A_1^{(2)}$	E
2058 (m)	1990 (m, sh)	1938 (st)

Generally, three infrared active stretch vibrations are predicted for complexes of the type $(CO)_5ML$ which belongs to the C_{4v} point group. These are two A_1-vibrations and an E-vibration. The B_1-vibration is only active in the Raman spectrum or for distorted

structures. In this case the $A_1^{(2)}$-band appears as a shoulder to the E-band at a lower frequency.[54]

2.2.3 Synthesis of complex 2

Fischer-type carbene complex **2** was prepared by adding phenyllithium (**2**) to a suspension of $W(CO)_6$ (**2**) in diethyl ether at room temperature. This was followed by alkylation with $(CH_3)_3O^+BF_4^-$ in water and extraction of the resulting carbene complex with pentane. The synthesis was completed by amminolysis of the carbene complex with 2-aminothiazoline in CH_2Cl_2 at room temperature (Scheme 2.19).



2

Scheme 2.19

[54] (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432. (b) L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

The product **2** was subsequently cooled to –30°C in a 1:3 CH_2Cl_2/pentane solution. Dark red single crystals were obtained. This compound is stable in the absence of air and moisture and decomposes slowly in solution. It is soluble in polar organic solvents, and less so in non-polar solvents.

No similar complexes have been reported in the literature.

2.2.4 Structure of complex 2

The single crystal X-ray structure determination of **2** yielded a surprising result (Figure 2.6). The hydrogen atom that was expected to be bound to N1 has migrated to N2. No structure similar to this one has been found in the Cambridge Crystallographic Data Center (CCDC). However, many compounds in which the thiazolinyl moiety occurs in a number of different resonance forms as a structural feature have been found. The data of a few representative complexes of this kind as well as that of a few aminocarbene complexes is summarized in Table 2.4. Selected bond lengths and angles for complex **2** are summarized in Table 2.5. The carbonyl ligands of tungsten are arranged octahedrally around the metal. (See Table 2.5 for the relevant data.) The W-C6 bond [2.013(4) Å] is shorter than the average of the other W-C bonds (2.047 Å). A look at other aminocarbene complexes (Table 2.4) has shown that this is the norm. The M-C1 bond is very long, at 2.252(4) Å, which is in accordance with other aminocarbene complexes, whose M-C1 bond lengths center around 2.2 Å. The C1-N1 bond is very short [1.315(5) Å] and this correlates with the data in Table 2.4. The lengthening of the W-C_{carb} bond and subsequent shortening of the C_{carb}-N bond can be explained by studying the resonance structures for complex **2** (Figure 2.7).

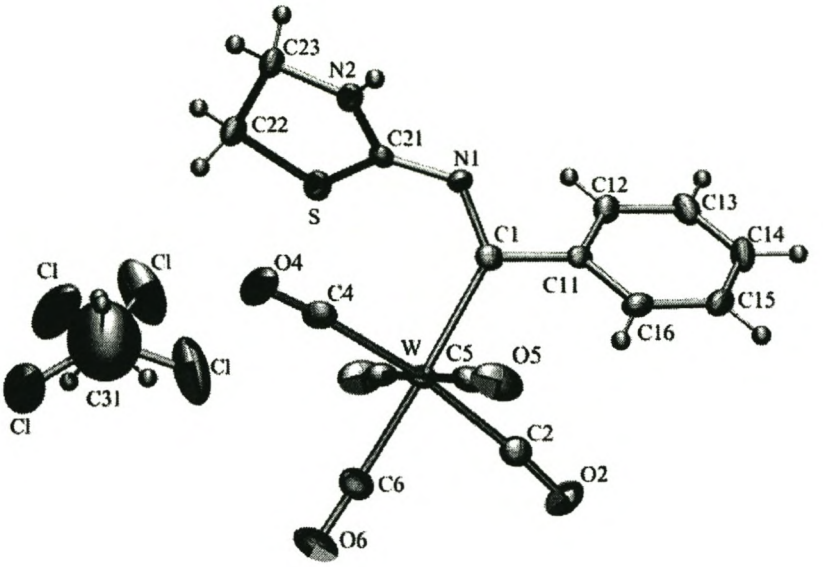
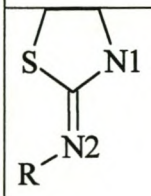
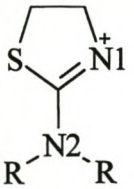
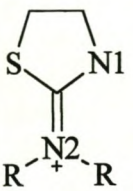
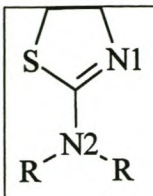
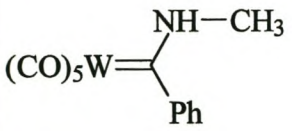
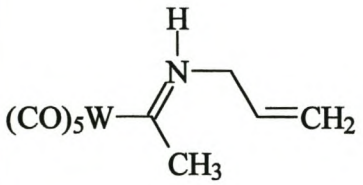
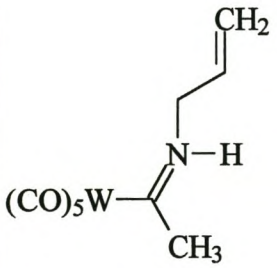
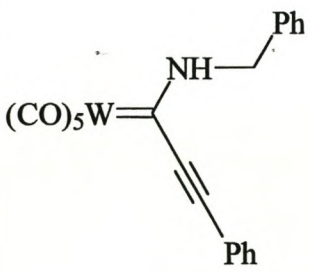
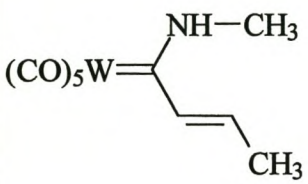
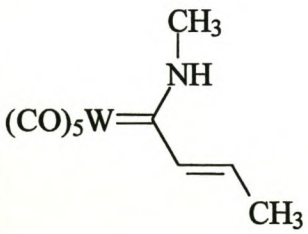


Figure 2.6: *The structure of complex 2*

Table 2.4: *Comparative data for complex 2*

Complex	Comments
	**i**[a,b,c] C-N1: 1.285, C-N2: 1.366, N-C-N: 122.232
	**ii**[d] C-N1: 1.308, C-N2: 1.308, N-C-N: 124.736
	**iii**[e] C-N1: 1.312, C-N2: 1.329, N-C-N: 126.330

	**iv**[f] C-N1: 1.345, C-N2: 1.286, N-C-N: 122.791
	**v**[g,h] W-C1: 2.186, W-C6: 1.950 W-C: 2.064, C1-N1:1.299
	**vi**[i] W-C1: 2.234, W-C6: 2.003 W-C: 2.037, C1-N1:1.307
	**vii**[i] W-C1: 2.206, W-C6: 2.011 W-C: 2.029, C1-N1:1.295
	**viii**[j] W-C1: 2.221, W-C6: 2.000 W-C: 2.047, C1-N1:1.311
	**ix**[k] W-C1: 2.243, W-C6: 2.004 W-C: 2.037, C1-N1:1.309
	**x**[k] W-C1: 2.242, W-C6: 1.970 W-C: 2.028, C1-N1:1.32

References are continued on the next page.

a The references for fragments **i – iv** are examples of representative structures.

b Bondlengths are in Å and angles are in degrees

c C. Cohen-Addad, *Acta Crystallogr., Sect. B*, 1982, **38**, 1753.

d V. Fernandez, M. Moran, J. C. Doadrio, E. Conradi, W. Willing and U. Muller, *Z. Naturforsch, Teil B*, 1987, **42**, 15.

e B. M. Vedavathi and K. Vijayan, *Acta Crystallogr., Sect B*, 1981, **37**, 475.

f. A. Bernalte-Garcia, F. J. Garcia-Barros, F. J. Higes-Rolando, A. M. Pizarro-Galan, C. Valenzuela-Calahorro, *Polyhedron*, 1997, **16**, 1137.

g C1 = Carbene carbon, C6 = Carbon trans to carbene carbon, W-C = Average length of W-C(*cis*) bonds.

h J. T. Guy, Jr. and D. W. Bennet, *Transition Met. Chem.*, 1984, **9**, 43.

i A. Parlier, H. Rudler, J. C. Daran and C. Alvarez, *J. Organomet. Chem.*, 1987, **333**, 245.

j R. Aumann, K. B. Roths, M. Fossmeier and R. Frohlich, *J. Organomet Chem.*, 1998, **556**, 119.

k B. A. Anderson, W. D. Wulff, T.S. Powers, S. Tribbitt and A. L. Rheingold, *J. Am. Chem. Soc.*, 1992, **114**, 10784.

Selected bond lengths and angles for complex **2** are summarized in Table 2.5. The carbonyl ligands of tungsten are arranged octahedrally around the metal. The W-C6 bond [2.013(4) Å] is shorter than the average of the other W-C bonds [2.047 Å]. A look at other aminocarbene complexes (Table 2.4) has shown that this is the norm. The M-C1 bond is very long, at 2.252(4) Å, which is in accordance with other aminocarbene complexes, whose M-C1 bond lengths center around 2.2 Å. The C1-N1 bond is very short [1.315(5) Å] and this correlates with the data in Table 2.4. The lengthening of the W-C_{carb} bond and subsequent shortening of the C_{carb}-N bond can be explained by studying the resonance structures for complex **2** (Figure 2.7).

Table 2.5: *Selected bond lengths and angles for complex* ***2***

Bond lengths / Å		Bond angles / degrees	
W-C1	2.252(4)	W-C1-N1	128.6(3)
W-C2	2.042(4)	W-C2-O2	174.2(4)
W-C3	2.061(5)	W-C3-O3	176.6(4)
W-C4	2.042(5)	W-C4-O4	173.6(4)
W-C5	2.041(5)	W-C5-O5	178.7(4)
W-C6	2.013(4)	W-C6-O6	177.3(4)
C1-N1	1.315(5)	C1-W-C2	94.33(15)
C2-O2	1.142(5)	C1-W-C3	88.24(15)
C3-O3	1.135(5)	C1-W-C4	93.33(15)
C4-O4	1.137(5)	C1-W-C5	90.78(15)
C5-O5	1.137(5)	C1-W-C6	6.26(16)
C6-O6	1.147(5)	C1-N1-C21	128.4(3)
C1-C11	1.504(5)	N1-C21-N2	123.1(4)
N1-C2	1.339(5)	N1-C21-S:	123.4(3)
C21-N2	1.312(5)	S-C21-N2:	112.8(3)
C21-S	1.739(4)	C21-N2-C2	115.6(3)
S-C22	1.822(4)	N2-C23-C22	105.8(3)
N2-C23	1.462(5)	C23-C22-S	104.7(3)
N2-H	0.880	C22-S-C21	90.41(19)
C22-C23	1.501(6)	N1-C1-C11	109.7(3)

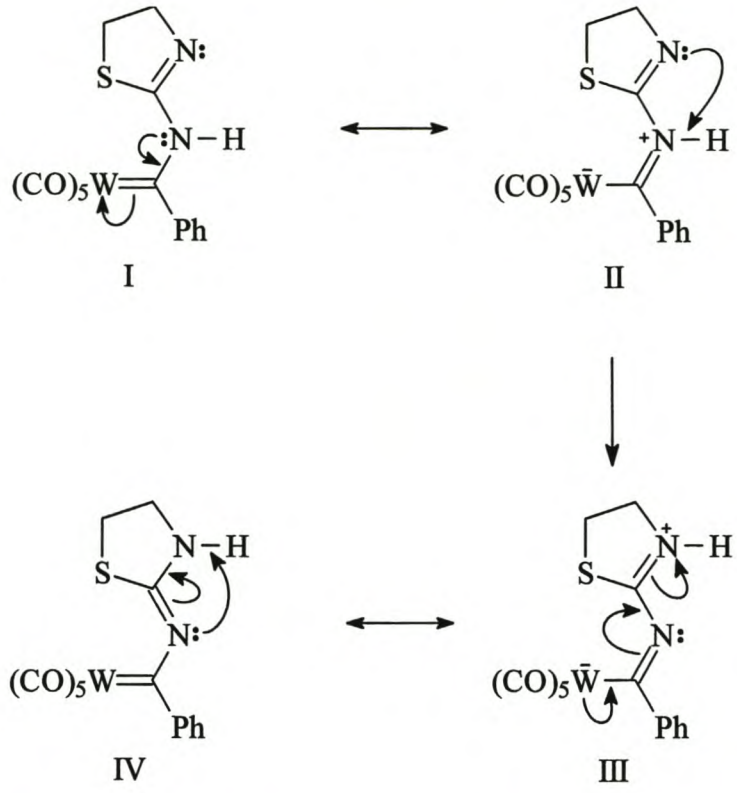


Figure 2.7: *Possible resonance structures for complex 2*

Although aminocarbene complexes are usually represented as in I, this is not the most important resonance form. When compared to the structure (Figure 2.6), it seems that structure II is the most important contributing structure. Obviously the ring nitrogen is also tje The bond lengths in the thiazolinyl ligand should be compared to the corresponding bond lengths of thiazolinyl ligands and substituents found in the CCDC. The bond length of C21-N1 is 1.339(5) Å and of C21-N2 is 1.312(5) Å. These lengths seem to confirm either one of structures I, II or III. Structure **iv** in Table 2.4 corresponds the best with the measured bond lengths of complex **2,** and since **iv** resembles resonance forms II and III, it can be assumed that this is indeed the configuration of complex **2**. Due to the similar chemical shifts in the NMR spectra of a series of these complexes (discussed later on in this chapter) it is probably safe to assume that this result also holds for other complexes synthesized in this study,

despite lack of crystallographic evidence. This is a rather unexpected result that is probably linked to the occurrence of hydrogen bonding in the solid state (Figure 2.8).

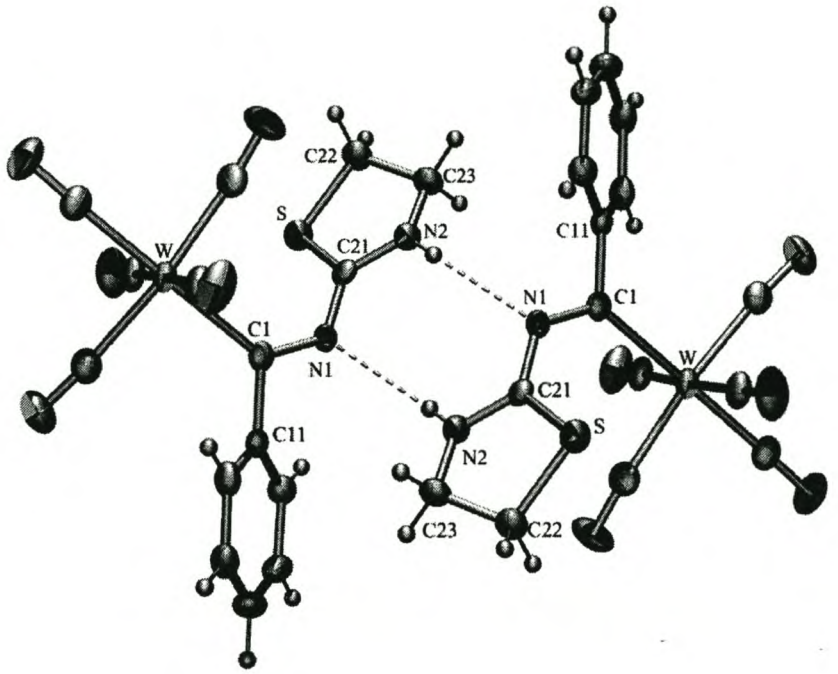


Figure 2.8: *Intermolecular hydrogen bonding in complex 2*

The hydrogen bonding occurs in such a way that an intermolecular six-membered ring is formed. It is hard to determine whether the hydrogen bonding occurs as a result of the hydrogen transfer, or *vice versa*. The most plausible explanation for this phenomenon is that it is a synergic process.

The molecular packing of complex **2** in the unit cell as viewed along the c-axis is shown in Figure 2.9. There are sixteen molecules per unit cell. They are packed in groups of four molecules each around the four symmetry centers within the unit cell. The groups are linked to each other by hydrogen bonding. The planes formed by the phenyl and the thiazolinyl intersect each other almost perpendicularly. The centers of symmetry are occupied by one dichloromethane molecule each.

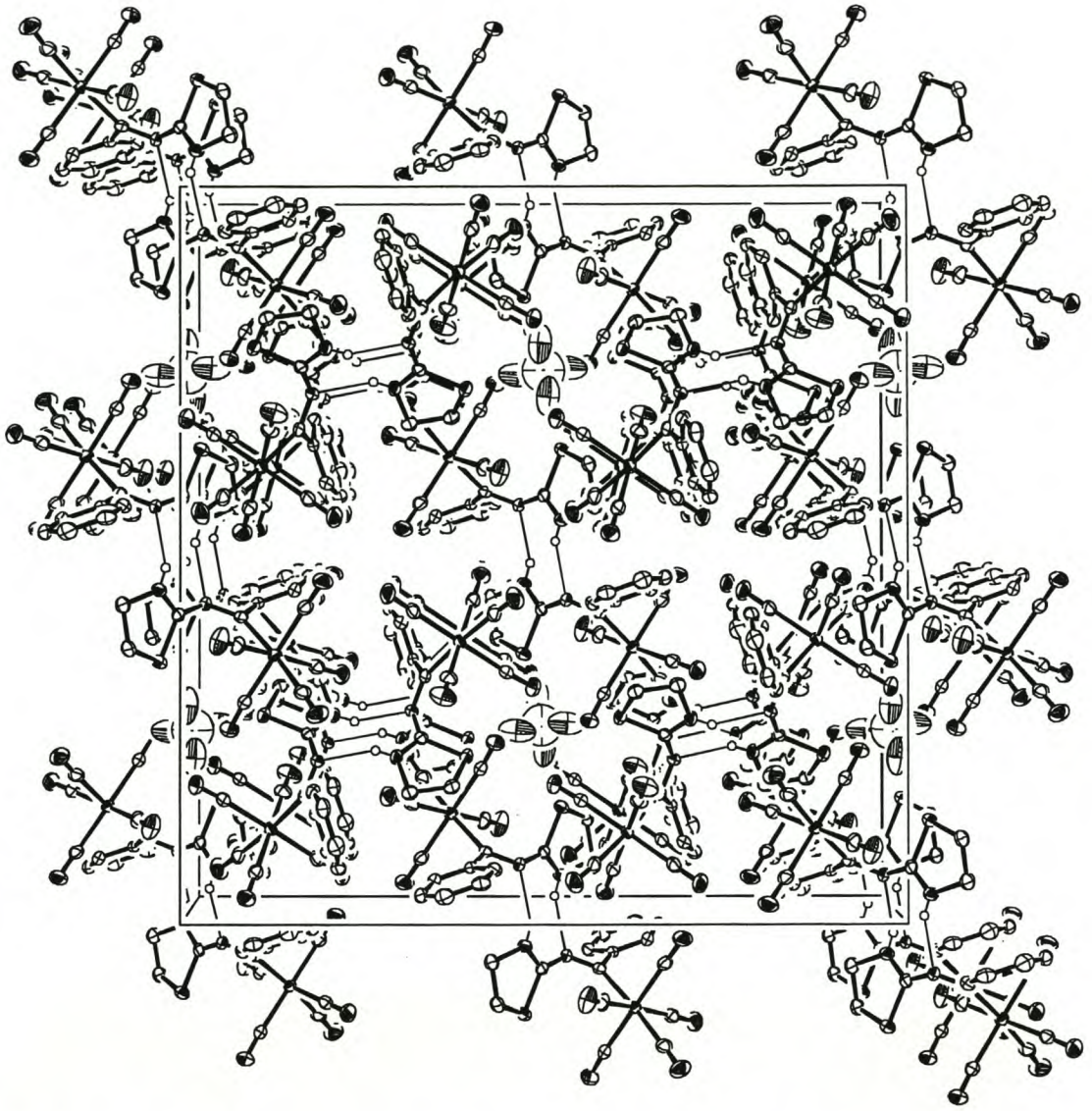


Figure 2.9: *The unit cell of complex* **2** *viewed along the c-axis, showing the hydrogen-bonding framework. All hydrogen atoms, except those involved in H-bonding, are omitted for clarity.*

The crystal data and refinement particulars for the X-ray crystallographic determination of the structure of complex **2** is summarized in Table 2.6

Table 2.6: *Crystal data and refinement particulars for complex* ***2***

Empirical formula	$C_{15}H_{10}N_2O_5SW¼CH_2Cl_2$
Formula weight	535.39
Temperature	173(2) K
Radiation, Wavelength	Mo K_α, 0.71073 Å
Crystal system, space group	Tetragonal, I $4_1/a$
Unit cell dimensions	a = 25.4487(6) Å, α = 90°, b = 25.4447(6) Å, β = 90° c = 10.7727(6) Å, γ = 90°
Volume	6975.7(3) $Å^3$
Z, calculated density	16, 2.039 g/cm^3
Reflections for cell parameters	14 104
Absorption coefficient	6.848 mm^{-1}
Absorption correction method	Semi-empirical (Scalepack)
T_{min}	0.279
T_{max}	0.356
F(000)	4 072
Crystal size	0.25 × 0.20 × 0.19 mm
Crystal Colour	Dark red
Diffractometer type	EnrafNonius KappaCCD
Scan type	Area detector
Theta range for data collection	2.26 to 27.47°
Index ranges	-33 ≤ h ≤ 22, -26 ≤ k ≤ 24, -12 ≤ l ≤ 13
Reflections collected / unique	14 104 / 3 969 [R(int) = 0.0600]
Refinement method	Full-matrix least squares on F^2

Table 2.6: *Continued*

Data / restraints / parameters	3 969 / 0 / 228
Goodness-of-fit on F^2 (S)	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0611
R indices (all data)	R1 = 0.0464, wR2 = 0.0654
Weighting scheme	Calcw = $1/[\sigma^2(Fo^2)+(0.0263P)^2]$ where P= $(Fo^2+2Fc^2)/3$
Maximum shift/esd	0.004

2.2.5 Spectroscopic characterization of complex 2

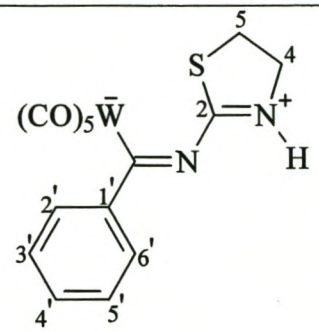
(i) NMR spectroscopy

The ^{1}H NMR and ^{13}C {^{1}H} NMR data for complex **2** is summarized in Table 2.7.

The peaks for H^4 and H^5 as well as N<u>H</u> appear at a lower field than in the ^{1}H NMR spectrum for the free ligand. This is due to the electron withdrawing effect of the carbene carbon atom. The electron withdrawing effect will be amplified because this complex has a very delocalized electron system. Two doublets for each of H^4, H^5 and N<u>H</u> occur. This can be ascribed to different orientations of the thiazolinyl group in the planar carbene ligand in solution. The signal for $H^{2'}$ and $H^{6'}$ is also doubled for the same reason. No double signals could be elucidated for the other aromatic protons.

Due to the delocalization of electron density to the M=C bond, most of the carbene substituent peaks in the ^{13}C NMR spectrum move to lower field. The occurrence of a peak at very low field, δ 280.4, indicates the presence of a carbene carbon atom. No isomerism could be detected in the ^{13}C NMR spectrum. This is probably due to the instability of the complex in solution. The intensity of the carbonyl signals are also very low.

Table 2.7: *^{1}H and ^{13}C-{^{1}H} NMR spectroscopic data for complex* **2**

Complex	 **2**
Solvent	CD_3COCD_3
N<u>H</u>	8.93 and 8.30 (1H. 2 x s)
H^4	4.64 (2H, t, J = 5.60) and 4.35 (2H, t, J = 7.86)
H^5	4.08 (2H, t, J = 8.32) and 3.91 (2H, t, J = 7.26)
$H^{2'}$ and $H^{6'}$	8.02 (2H, m) and 8.03 (2H, m)
$H^{3'}$ and $H^{5'}$	7.55 (2H, t, J = 7.55)
$H^{4'}$	7.72 (2H, t, J = 7.35)
M=<u>C</u>	280.4
CO_{trans}	200.0
CO_{cis}	194.5
C^2	169.1
C^5	37.1
C^4	64.7
$C^{1'}$	149.7
$C^{2'}$ and $C^{6'}$	130.2
$C^{3'}$ and $C^{5'}$	128.8
$C^{4'}$	133.0

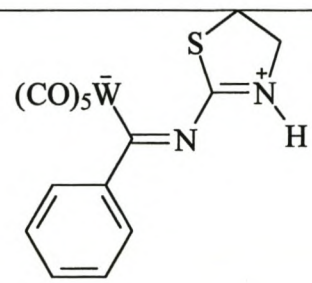
(ii) Mass spectroscopy

The mass spectroscopic data for complex **2** is summarized in Table 2.8.

The fragmentation of complex is characterized by the consecutive loss of five carbonyl ligands, followed by the phenyl and the metal ion. The molecular ion is at an intensity of 20%. Fragments containing tungsten appear as a cluster of peaks due to the many isotopes of the metal.

Table 2.8: *Mass spectroscopic data for complex 2*

Complex **2**



M/z	I	Fragment ion
514	20	M^+
486	31	$[M\text{-CO}]^+$
458	50	$[M\text{-2CO}]^+$
430	77	$[M\text{-3CO}]^+$
402	43	$[M\text{-4CO}]^+$
374	16	$[M\text{-5CO}]^+$
346	11	$[W{=}C(C_6H_5)C{=}NS]^+$
184	44	$[W]^+$
102	18	$[H_2NC{=}NCH_2CH_2S]^+$

(iii) Infrared spectroscopy

The ν(CO)-data for complex **2** is summarized in Table 2.9.

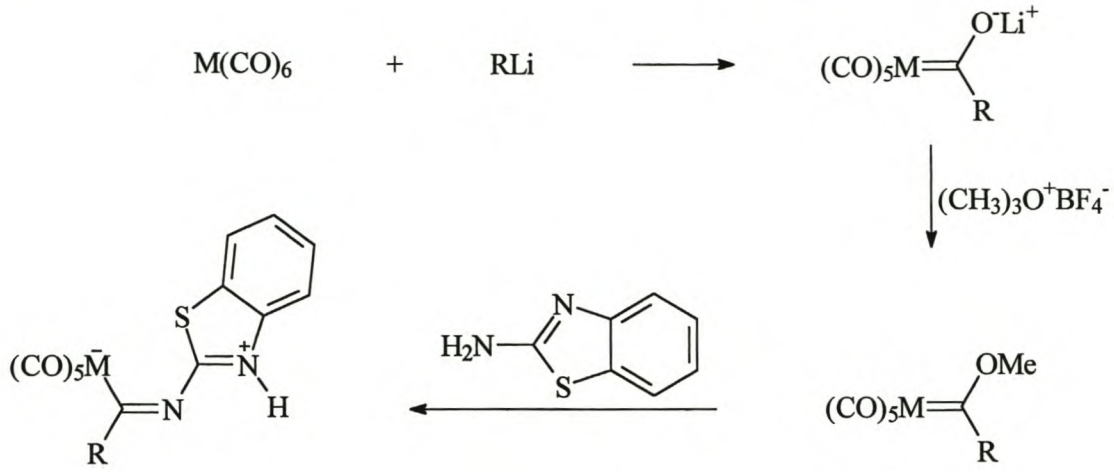
Table 2.9: *ν(CO) data for complex 2*

ν(CO)/cm^{-1}			
$A_1^{(1)}$	B_1	$A_1^{(2)}$	E
2063 (w)	2010 (w)	1938 (st, sh)	1921 (st)

It has been said earlier in this chapter that the B_1 vibration for the $(CO)_5ML$ complex is only active in Raman spectroscopy, because this kind of complex belongs to the C_{4v} point group. However, if the ligand L causes distortion in the square pyramidal plane of the four *cis*-carbonyls by steric hindrance, the complex approaches a D_{2d}-type structure. In these cases a weak B_1-band becomes visible.[55] The occurrence of a B_1-band in complex **2** shows that distortion does take place. The $A_1^{(2)}$-band occurs as a shoulder at higher frequency than the E-band.

2.2.6 Synthesis of complexes 3,4 and 5

Fischer-type carbene complexes **3 - 5** were synthesized by adding methyllithium (**3**) or phenyllithium (**4,5**) to a suspension of $Cr(CO)_6$ (**3,4**) or $Mo(CO)_6$ (**5**) in ether at room temperature. This was followed by alkylation with $(CH_3)_3O^+BF_4^-$ in water and extraction of the resulting carbene complex with pentane. The synthesis was completed by amminolysis of the carbene complex with 2-aminobenzothiazole in CH_2Cl_2 at room temperature (Scheme 2.20).



	M	R
3	Cr	Me
4	Cr	Ph
5	Mo	Ph

Scheme 2.20

The aminolysis was done in CH_2Cl_2 and not in the more usual pentane because 2-aminobenzothiazole and 2-aminothiazoline are not soluble in nonpolar solvents. They are therefore never present in sufficient concentration to react with the oxycarbene. A variety of solvents were tested and dichloromethane gave the best results.

The products **3 - 5** were purified by column chromatography using different ratios of CH_2Cl_2 and hexane as eluent. Removal of the solvent yielded orange microcrystals of **3** and **4**; and red micro-crystals of **5**. These complexes are soluble in most polar organic solvents and less so in nonpolar solvents. They are stable in the absence of moisture and air, and seem to be moderately stable even in the presence of air. However, complexes **3 - 5** decompose slowly in solution.

No examples of similar aminocarbene complexes have been found in the literature.

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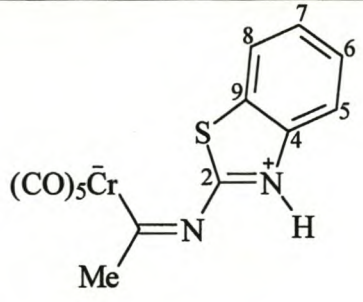
[55] (a) P. S. Braterman, *Metal Carbonyl Spectra*, Academic Press, London, 1975. (b) M. Parikowski and M. Bigorgne, *J. Organomet. Chem.*, 1969, **19**, 393.

2.2.7 Spectroscopic characterization of complexes 3 - 5

(i) NMR spectroscopy

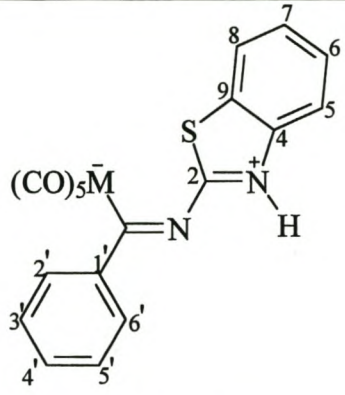
The ^{1}H NMR data for complexes **3 - 5** is summarized in Table 2.10. The peaks for H^5, H^6, H^7, H^8 as well as N<u>H</u> appear at lower field than in the free ligand due to the electron withdrawing effect of the carbene carbon atom. Although isomerism is expected in these compounds, it is not seen in either the ^{1}H or the ^{13}C NMR spectra. This is probably due to these compounds instability in solution (even at low temperatures, samples left overnight showed visible signs of decomposition), as well as the tendency of aminocarbene complexes to form mostly in the *syn* configuration.[56] Different deuterated solvents were tested, as well as a range of running times for the NMR experiments. The complexes were the most stable in acetone. The optimal length for the NMR experiments were about three to four hours, before decomposition of the complexes obscured the results.

Table 2.9: *^{1}H NMR data for complexes **3 - 5***

Complex	 **3**
Solvent	CD_3COCD_3
N<u>H</u>	8.20 (1H, s)
H^8	8.46 (1H, m)
H^7	7.76 (1H, t, J = 7.45)

[56] E. Moser and E. O Fischer, *J. Organomet Chem.*, 1969, **16**, 275.

Table 2.9: *Continued*

H^6	7.68 (1H, t, J = 7.75)	
H^5	8.26 (1H, m)	
Me	3.55 (1H, s)	
Complex	 **M** **4** Cr **5** Mo	
Complex	**4**	**5**
Solvent	CD_3COCD_3	CD_3COCD_3
N<u>H</u>	7.93 (1H, s)	9.25 (1H, 2 x s)
H^8	8.12 (1H, m)	8.59 (1H, 2 x m)
H^7 and H^6	7.62 (2H, m)	8.19 (2H, m)
H^5	8.06 (1H, m)	8.46 (1H, 2 x m)
$H^{2'}$ and $H^{6'}$	7.71 (2H, m)	8.30 (2H, m)
$H^{3'}$ and $H^{5'}$	7.34 (2H, m)	7.96 (2H, m)
$H^{4'}$	7.57 (1H, m)	8.11 (2H, m)

The ^{13}C-{^1H} NMR data for complexes **3 - 5** is summarized in Table 2.11. Due to the delocalization of electron density to the M=C bond, many of the carbene substituent peaks move to a lower field. The occurrence of a peak at very low field indicates the presence of a carbene carbon atom.

Table 2.11: *^{13}C-{^{1}H} NMR data for complexes* ***3 - 5***

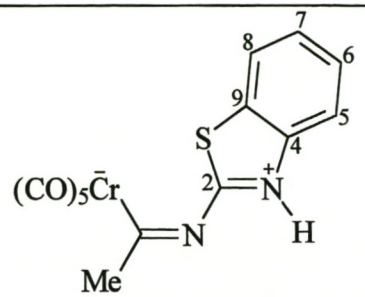
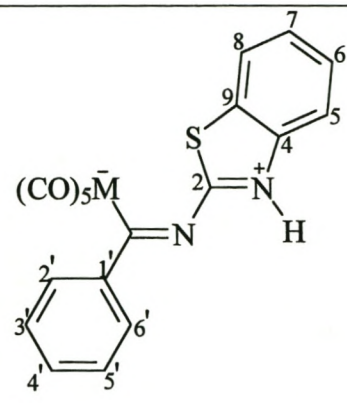
Complex	 **3**
Solvent	CD_3COCD_3
M=<u>C</u>	312.0
CO_{trans}	217.0
CO_{cis}	211.7
C^2	160.6
C^9	132.3
C^4	149.9
C^5	123.1
C^6	127.2
C^7	125.6
C^8	120.3
Me	36.5

Table 2.11: *Continued*

Complex		**M** **4** Cr **5** Mo

Complex	**5**	**6**
Solvent	CD_3COCD_3	CD_3COCD_3
M=C	307.4	368.3
CO_{trans}	215.4	205.4
CO_{cis}	206.3	201.2
C^2	163.7	170.1
C^9	132.7	133.0
C^4	144.5	151.5
C^5	124.8	123.1
C^6	127.5	127.2
C^7	127.3	126.0
C^8	122.0	122.7
$C^{1'}$	151.7	152.4
$C^{2'}$ and $C^{6'}$	130.2	130.8
$C^{3'}$ and $C^{5'}$	129.0	129.1
$C^{4'}$	134.4	134.5

(ii) Mass spectroscopy

The mass spectroscopic data for complexes **3** and **4** is summarized in Table 2.12. Complex **5** shows no molecular ion or consistent fragmentation pattern and is therefore not included. The fragmentation of complexes **3** and **4** follows the pattern of consecutive loss of the carbonyl ligands followed by the loss of the metal, splitting of the remaining fragment and fragmentation of the benzothiazole moiety. The fragmentation of the 2-amino-benzothiazole ligand occurs in the same manner as that of the free molecule.

Table 2.12: *Mass spectroscopic data for complexes **3** and **4***

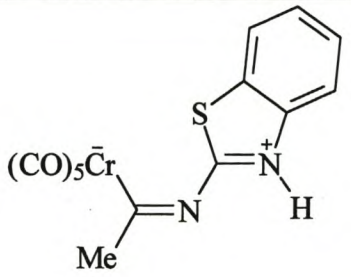
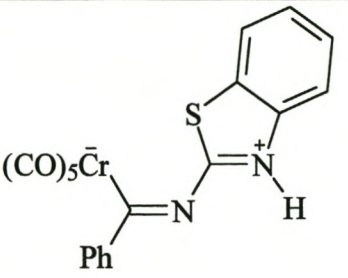
Complex	 **3**	
m/z	I[a]	Fragment ion
368	5	M^+
340	2	$[M\text{-CO}]^+$
312	2	$[M\text{-2CO}]^+$
284	7	$[M\text{-3CO}]^+$
256	15	$[M\text{-4CO}]^+$
228	56	$[M\text{-5CO}]^+$
170	47	$[CH_3CNHC{=}NC_6H_4S\text{-}o]^+$
150	25	$[H_2N\text{-}C{=}NC_6H_4S\text{-}o]^+$
108	39	$[S\text{-}C_6H_4]^+$

Table 2.12: *Continued*

80	69	$[Cr{=}C{=}CH_2]^+$
52	100	$[Cr]^+$
28	63	[CO]
Complex  **4**		
m/z	I^a	Fragment ion
430	18	M^+
402	8	$[M\text{-}CO]^+$
374	3	$[M\text{-}2CO]^+$
346	19	$[M\text{-}3CO]^+$
318	59	$[M\text{-}4CO]^+$
290	42	$[M\text{-}5CO]^+$
238	31	$[H_5C_6CNHC{=}NC_6H_4S\text{-}o]^+$
150	22	$[H_2N\text{-}C{=}NC_6H_4S\text{-}o]^+$
108	33	$[S\text{-}C_6H_4]^+$
32	17	$[Cr]^+$
28	36	[CO]

(iii)Infrared spectroscopy

The ν(CO) data for complexes **3 - 5** is summarized in Table 2.13.

Table 2.13: *ν(CO) data for complexes **3 - 5***

Complex	ν(CO)/cm^{-1}			
	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E
3	2058 (m)	-	1980 (m, sh)	1936 (st)
4	2059 (m)	-	1995 (m, sh)	1946 (st)
5	2071 (m)	2019 (w)	1981 (m, sh)	1935 (st)

Distortion plays a role in the configuration if the Mo-complex (**5**) as can be seen from the presence of the B_1-vibration in both cases. The B_1-vibration is absent from the spectra of the Cr-complexes (**3, 4**) which indicates that there is little, if any distortion of the *cis*-CO-ligands from the square pyramidal plane. In all the cases $A_1^{(2)}$ occurs as a shoulder at higher frequency to the E-band.

2.3 Conclusion

In the synthesis of these complexes, a number of interesting observations were made and quite a few possibilities for further investigation have arisen. In the case of complex **1** the difference in stability of the precursor complex and the aminocarbene is quite startling. Attempts have been made to synthesize similar complexes utilizing 4-methylthiazole as ligand, but it was not successful.

In the case of complexes **2 – 5** the formation of the complexes was surprising, given the steric bulk of the amino ligands. However, it was found that the complexes decomposed if stirred for too long a period, an observation that correlates with their

lability if left in solution. Nevertheless, these complexes are quite stable in the solid state, with the exception of the molybdenum analogues. Several attempts have been made to synthesize other molybdenum complexes of this type, but it was not successful. Another surprise was the migration of the hydrogen atom in the thiazolinyl ligand. It is unfortunate that more crystals could not be obtained in order to see whether this happens to the other complexes too, although, judged by the similar shifts in the NMR spectra of the complexes it is highly probable. The thiazoline complexes are less stable than the benzothiazole complexes, and they are also more difficult to purify. Attempts were also made to synthesize complexes with 2-aminobenzimidazole, but it was an unmitigated failure. Maybe, since the reaction works with thiazoles, oxazoles may also prove to be useful as ligands in this kind if carbene complex. However, it is clear from the work done in this study that there is great potential to expand the range of carbene complexes that can be used in organic synthesis by making use of a diverse range of ligands.

2.4 Experimental

2.4.1 General

All reactions were performed under positive nitrogen pressure with a standard vacuum line and Schlenk techniques.[57] Glassware was dried at 120° for a minimum of two hours and cooled under vacuum before use. Manipulations at low temperatures were done by placing the reaction flask in a propanol bath cooled by dry ice or liquid nitrogen.

[57] D. F. Schriver, *Manipulation of Air-sensitive Compounds*, McGraw-Hill, New York, 1969.

All solvents were dried as follows: Dichloromethane, toluene, pentane, hexane and diethyl ether for two days minimum on potassium hydroxide and for at least two days on 3Å molecular sieves; THF for four days on potassium hydroxide. All the solvents were subsequently distilled in an inert atmosphere; dichloromethane over calcium hydride, and pentane, hexane toluene, diethyl ether and THF over sodium wire, tetraglyme and benzophenone.[58]

Separations by means of column chromatography[59] were done under a nitrogen atmosphere with kieselgel 60 (particle size 0.063 – 0.200 mm) from Merck as stationary phase. Double sided columns were used for low temperature separations. Before use, the stationary phase was washed with diethyl ether and dried under vacuum for 12 hours. Thin layer chromatography (Alugram Sil G/U_{154}) was used to follow the progress of reactions.

All ^{1}H and ^{13}C NMR spectra were recorded in deuterated acetone with a Varian VXR 300 spectrometer at 25°C. Mass spectra were recorded with a AMD 604 spectrometer. A Perkin Elmer 1600 Series FTIR was used to determine infrared spectra of solutions in dichloromethane.

All metal carbonyls, methyllithium (1.6M in diethylether), 2-aminothiazoline, 2-aminobenzothiazole and thiazole were purchased from Aldrich and used without further purification.

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[58] (a) D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1985. (b) A. Salzer in *Synthetic Methods of Organometallic and Inorganic Chemistry (Hermann/ Brauer)*, **1**, (W. A. Harmann, A. Salzer: Eds), Georg Thieme, NY, 1996. (c) R. J. Errington, *Advanced Practical Inorganic and Metalorganic Chemistry*, Chapman & Hall, 1997.

[59] (a) W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.*, 1978, **43(14)**, 2923. (b) K. A. M. Kremer, P. Helquist, *Organometallics*, 1984, **3**, 1743.

2.4.2 Synthesis of complex 1

Benzothiazole (0.550 cm^3, 1.250 g/cm^3, 5.0 mmol) was dissolved in THF (40 cm^3) and cooled to –78°C. Standardized buthyllithium in hexane (3.17 cm^3, 1.6M, 5.0 mmol) was slowly added. The orange solution was stirred at –78°C for 30 minutes. Chromium hexacarbonyl (1.100 g, 5.0 mmol) was suspended in THF (50 cm^3) and cooled to –78°C. The *in situ*-prepared benzothiazol-2-lithium was slowly added to the $Cr(CO)_6$ and the reaction mixture turned dark red. The solution was stirred for 2.5 hours at –78°C after which the mixture was allowed to reach room temperature slowly. The solvent was removed under vacuum, the dark brown residue washed with 3 portions of 20 cm^3 hexane, dissolved in CH_2Cl_2 (60 cm^3) and alkylated at –20°C with CF_3SO_3Me (0.57 cm^3, 1.45 $g.cm^{-3}$, 5.0 mmol). The reaction mixture was stirred at –20°C for 30 minutes, slowly heated to room temperature and stirred for an additional 30 minutes.[52]

After filtering through a plug of silica, the reaction mixture was cooled down to 0°C and ammonia was bubbled through for 30 minutes whilst stirring. The solution was stirred for an additional 30 minutes and allowed to attain room temperature slowly.[23] The solvent was removed and the product transferred to a cold (-15°C) silica gel column and eluted with CH_2Cl_2/hexane (1:1). The red fraction was collected. Removal of the solvent yielded the red product **1**. Redissolving in CH_2Cl_2 and layering with pentane, cooling down to –30°C yielded red micro crystals of **1**.

Yield: 0.443 g (25 %)

2.4.3. Synthesis of complex 2

Pentacarbonyltungsten(0)phenylmethoxy carbene[60] (2.220 g, 5.0 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and 2-aminothiazoline (1.533 g, 15 mmol) was added. The reaction mixture was stirred for 15 minutes at room temperature and the solvent removed. Redissolving in CH_2Cl_2 and layering with pentane yielded red microcrystals of **3**.

Yield: 0.694 g (27 %)

2.4.4. Synthesis of complex 3

Pentacarbonylchrom(0)methylmethoxy carbene[60] (1.251 g, 5.0 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and 2-aminobenzothiazole (1.533 g, 15 mmol) was added. The reaction mixture was stirred for 30 minutes at room temperature and the solvent removed. After filtering through a plug of silica, the solvent was removed and the product transferred to a cold (-15°C) silica gel column and eluted with CH_2Cl_2/hexane (3:2). The orange fraction was collected. Removal of the solvent yielded the orange product **4**.

Yield: 0.368 g (25 %)

2.4.5. Synthesis of complex 4

Pentacarbonylchrom(0)phenylmethoxy carbene[60] (1.560 g, 5.0 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and 2-aminobenzothiazole (1.533 g, 15 mmol) was added. The reaction mixture was stirred for 30 minutes at room temperature and the solvent removed. After filtering through a plug of silica, the solvent was removed and the product transferred to a cold (-15°C) silica gel column and eluted with CH_2Cl_2/hexane

[60] S. Komiya (ed.), *Synthesis of Organometallic Compounds (A Practical Guide)*, John Wiley & Sons, New York, 1997.

(1:1). The red fraction was collected. Removal of the solvent yielded the red product **3**. Redissolving in CH_2Cl_2 and layering with pentane yielded red microcrystals of **3**.

Yield: 0.430 g (25 %)

2.4.6. Synthesis of complex 5

Pentacarbonylmolybdenum(0)phenylmethoxy carbene[60] (1.775 g, 5.0 mmol) was dissolved in CH_2Cl_2 (40 cm^3) and 2-aminobenzothiazole (1.533 g, 15 mmol) was added. The reaction mixture was stirred for 30 minutes at room temperature and the solvent removed. After filtering through a plug of silica, the solvent was removed and the product transferred to a cold (-15°C) silica gel column and eluted with CH_2Cl_2/hexane (2:1). The red fraction was collected. Removal of the solvent yielded the red product **5**. Redissolving in CH_2Cl_2 and layering with pentane yielded red microcrystals of **5**.

Yield: 0.247 g (12 %)

2.4.7 Structure of complex 2

The crystal and molecular structure of complex **2** was determined by Dr. J. Bacsa (Department of Chemistry, University of Cape Town) and M. Esterhuysen (Department of Chemistry, University of Stellenbosch). A red crystal was mounted on a glass fibre and transferred to an Enraf-Nonius KappaCCD -diffractometer. The data was collected with monochromatic Mo-K_α-radiation of wavelength $\lambda = 0.71073$Å and corrected for Lorenz and polarization effects. The position of the heaviest atom was determined by a Patterson synthesis and anisotropic displacement parameters were used for all the other atoms with the exception of the hydrogen atoms. The computer

program SHELX-97 was used for the determination of the structure and the refinement of the atomic coordinates. Additional information can be obtained from M. Esterhuysen, department of Chemistry, University of Stellenbosch, Stellenbosch.

synthesize Cp_2TiCl_2 and Cp_2ZrCl_2.[5] It has been found that the halide ions in Cp_2MCl_2 (M = Ti, Zr) can easily be exchanged for Br^- or I (Scheme 3.1).[6]

$$3\ Cp_2MCl_2 + 2\ BX_3 \longrightarrow 3\ Cp_2MX_2 + 2\ BCl_3$$

$$X = Br^-, I^-$$

Scheme 3.1

(ii) Structure

In all cases, the structure of Cp_2MX_2 (M = Ti, Zr; X = Cl, Br) is that of a bent sandwich with the X ligands perpendicular on the plane formed by the cyclopentadienyl ligands and the central metal atom. The X-M-X angle depends on the d-electron configuration of the metal and usually is between 85° and 88°.[7] This configuration has also been borne out by molecular orbital calculations.[8] The Cp-M-Cp angle remains constant at 130°. This is probably due to steric hindrance and repulsion between the Cp ligands. The ligand X determines whether the Cp ligands are staggered or eclipsed since both conformations are energetically possible (Figure 3.1).[9]

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[5] (a) C. L. Sloan and W. A. Barber, *J. Am. Chem. Soc.*, 1959, **81**, 1364. (b) A. F. Reid and P. C. Wailes, *J.Organomet. Chem.*, 1964, **2**, 329.
[6] P. M. Druce, B. M. Kingstrom, M. F. Lappert, T. R. Spalding and R. C. Srivastava, *J. Chem. Soc. (A)*, 1969, 2106.
[7] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Crystallogr.*, 1974, **B30**, 2290.
[8] J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
[9] M. A. Bush and G. A. Sim, *J. Chem. Soc. (A)*, 1971, 2225.

(a) *(b)*

Figure 3.1 *(a) Bis(cyclopentadienyl)zirconium fluoride*

(b)Bis(cyclopentadienyl)zirconium chloride

(iii) Reactions of bis(cyclopentadienyl)titanium and –zirconium dihalides

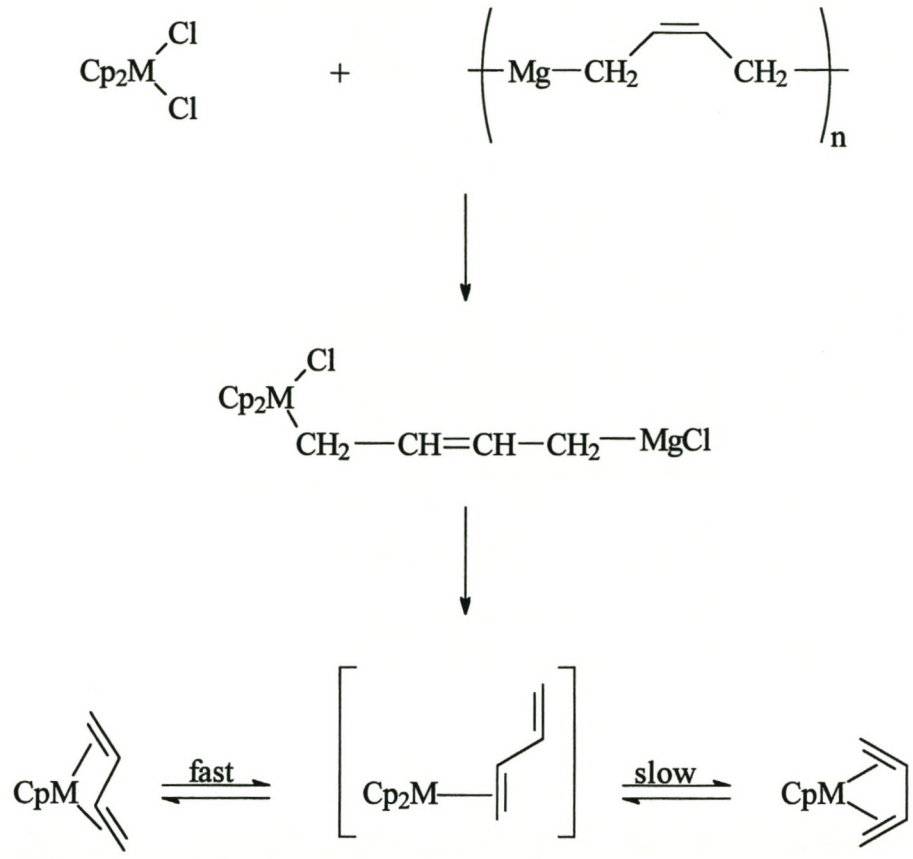
When bis(cyclopentadienyl)titanium and –zirconium dihalides undergo photolysis, intermolecular exchange of cyclopentadienide radicals occur.[10] Under kinetic control, the reaction of magnesium butadiene with Cp_2MCl_2 (M = Ti, Zr) complexes gives (s-trans-η^4-butadiene)-metallocene complexes (Scheme 3.2).[11]

Titanocenes are used in C-H activation. An example is thermolysis in aromatic hydrocarbon solvents where diarylzirconocenes and –titanocenes undergo successive replacement of their σ-bonded ligands by arylgroups of the solvent (Scheme 3.3).[12]

[10] (a) J. M. O'Connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307. (b) E. Vitz and C. H. Brubaker, Jr., *J. Organomet. Chem.*, 1974, **82**, C16. (c) M. Pong and C. H. Brubaker, Jr., *J. Organomet. Chem.*, 1977, **135**, 333.

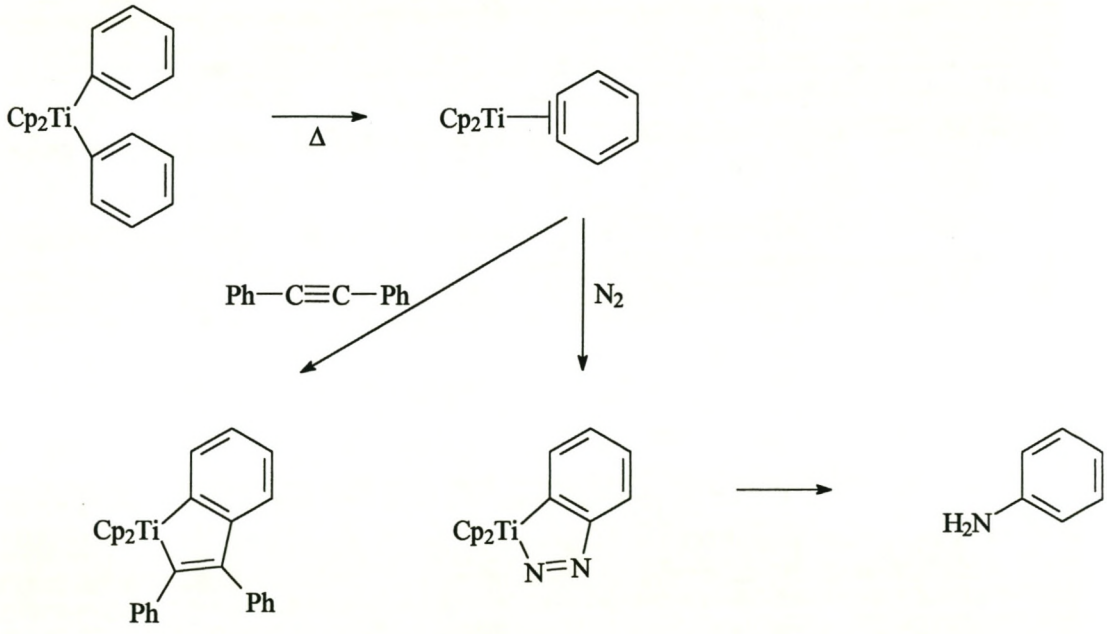
[11] U.Dorf, K. Engel and G. Erker, *Organometallics*, 1983, **2**, 462.

[12] G. Erker, *J. Organomet. Chem.*, 1977, **134**, 189.



M = Ti, Zr

Scheme 3.2

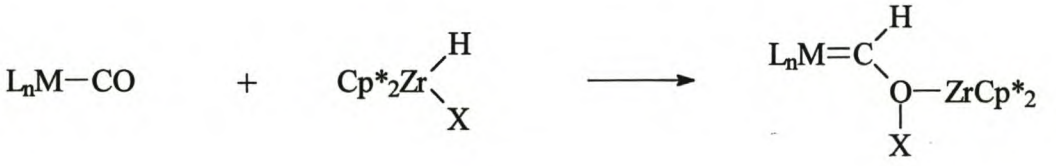


Scheme 3.3

3.1.2 Bimetallic systems

(i) Metal carbonyl to metal carbene transformation

Although metal carbene complexes are probably among the most versatile organo-metallic reagents for the synthesis of organic compounds, the synthesis by Fischer and Maasböl[13] has remained the most important way of preparing these compounds for a long time. However, it has been discovered by Erker *et al.*[14] that bis(cyclopenta-dienyl)zirconium derivatives can be used to convert metal carbonyls into metal car-bene complexes (Scheme 3.4). This method of synthesis makes it possible to prepare a greater range of metal carbene complexes than originally thought possible.[15]



Scheme 3.4

An extension of the reaction in Scheme 3.3 can be used to prepare cyclic carbene complexes of the Group VI metals (Scheme 3.5).[16] This is an interesting variation from Fischer's original route to heteroatom substitution. Sometimes the two-step path of the classical synthesis is unsuitable due to side reactions at the stage of the acylmetalate.[17]

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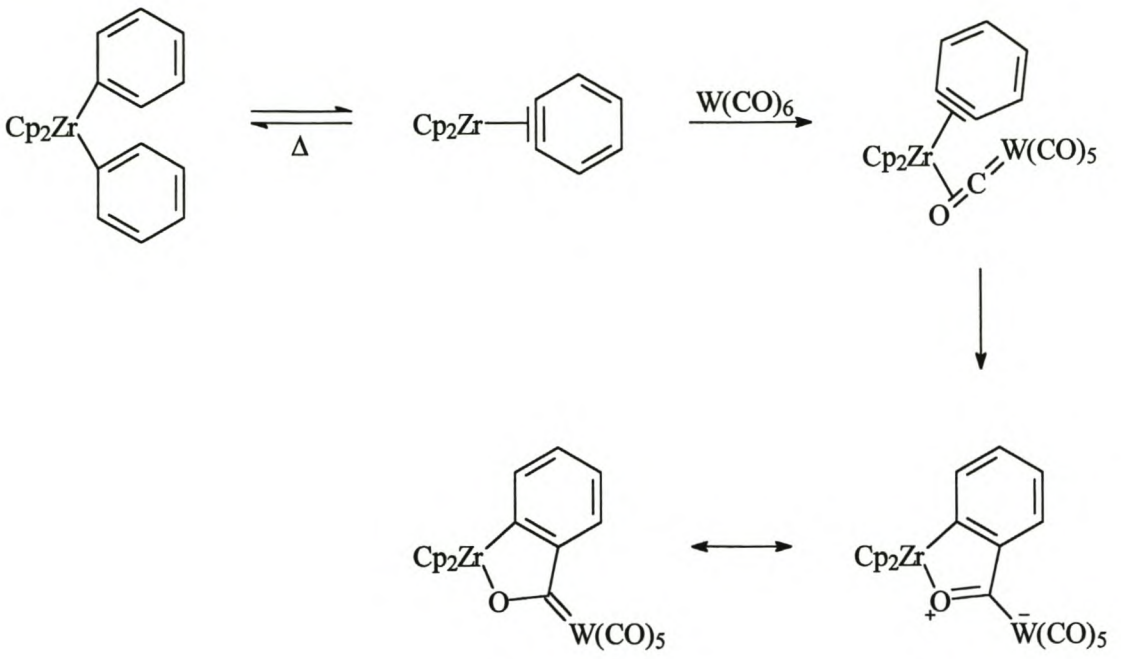
[13] E. O. Fischer and A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, 1964, **3**, 580.
[14] G. Erker and R. Lecht, *J. Orgamomet. Chem.*, 1986, **311**, 45.
[15] (a) J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729. (b) L. Zhu and M. Kostić, *J. Organomet. Chem.*, 1987, **335**, 395.
[16] G. Erker, U. Dorf, R. Mynott, Y.-H. Tsay and C Krüger, *Angew. Chem. Int. Ed. Engl.*, 1985, **24(7)**, 584.
[17] C. M. Jensen, C. B. Knobler and H. D. Kaesz, *J. Am. Chem. Soc.*, 1984, **104,** 5926.

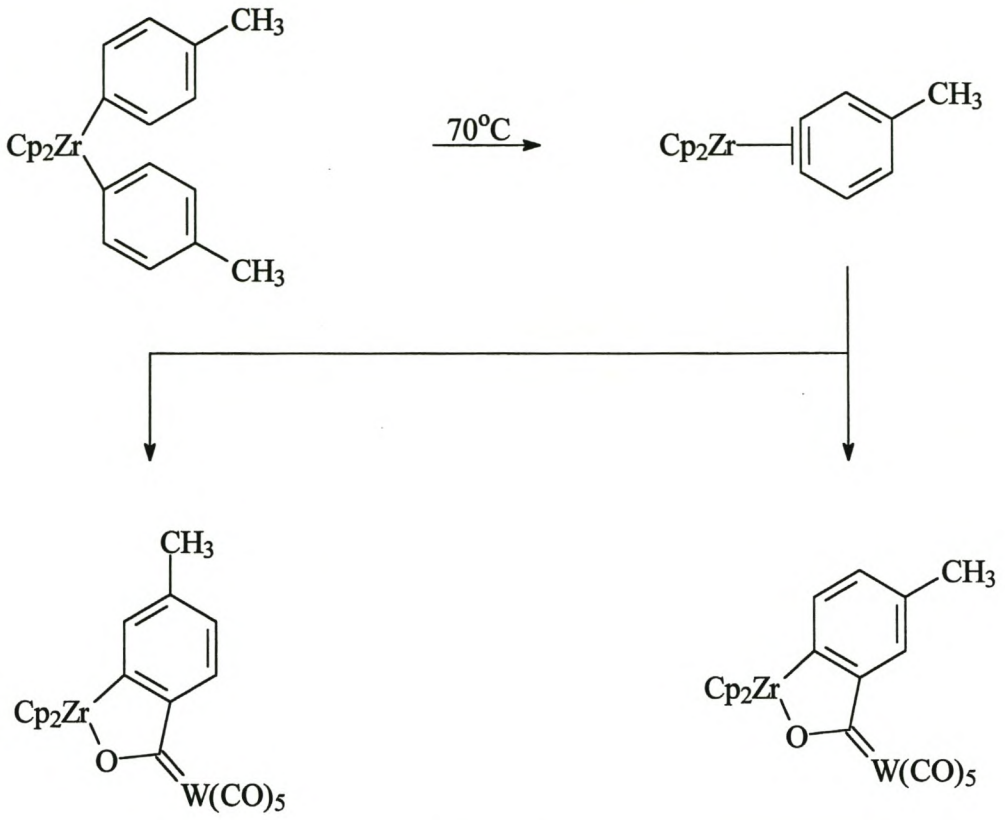


Scheme 3.5

If a substituted phenyl group is used as substituent in the above-mentioned reaction, a mixture of two products is possible (Scheme 3.6).[18]

Another useful reagent for the preparation of metal carbene complexes is butadiene zirconocene, referred to in the previous section.[11] It exists at room temperature as two stable, isolable isomers (Figure 3.2) The energy needed for interconversion between these two isomers is about 22.7 kcal/mol.[19] These two isomers show different chemical behaviour.[20] The *cis*-isomer reacts as a metal alkyl and readily adds to carbonyl bonds in a similar way to a carbon nucleophile. The *trans*-isomer, on the other hand, undergoes non-nucleophilic C-C-coupling reactions *via* a η^2-diene metal-

[18] G. Erker, *Polyhedron*, 1988, **7(22)**, 2451.
[19] G. Erker, K. Engel and C.Krüger, *Chem. Ber.*, 1982, **115**, 3300.
[20] G. Erker, K. Engel, J. L. Atwood and W. E. Hunter, *Angew. Chem.* 1983, **95**, 506.



Scheme 3.6

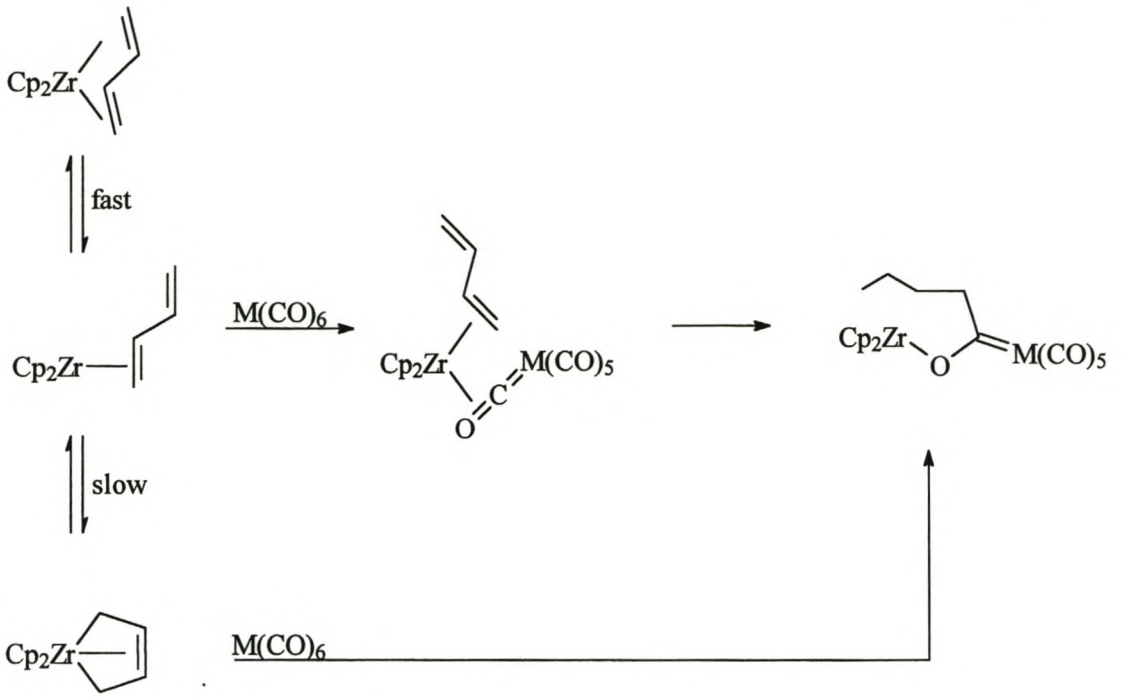
(a) *(b)*

Figure 3.2 *(a) s-cis-η^4-butadiene zirconocene*

(b) s-trans-η^4-butdiene zirconocene

locene intermediate. $Cr(CO)_6$ reacts slowly with an equilibrium mixture of these two isomers at room temperature. (Scheme 3.7).[21]

[21] (a) G. Erker and U. Dorf, *Angew. Chem. Int. Ed. Engl.*, 1983, **22,** 777, 1066. (b) G. Erker, U. Dorf, R. Benn, R.-D. Reinhardt and J. L. Petersen, *J. Am. Chem. Soc.*, 1984, **106**, 7649.

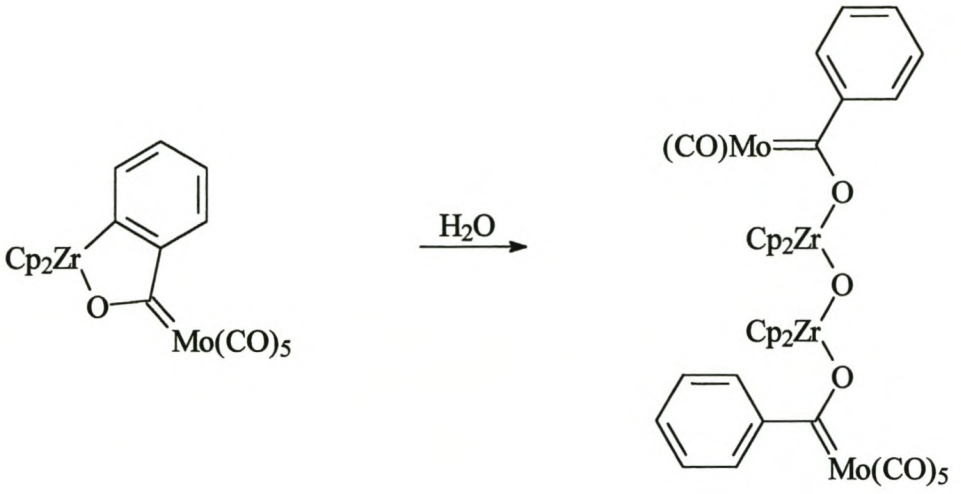


M = Cr, Mo, W

Scheme 3.7

Usually, a side reaction occurs in which the metallocene reacts with the carbonyl to yield a metallacyclic adduct.[22] Reactions of the same kind can be performed with ketones,[23] resulting in highly stereospecific products. Open chain multi-nuclear M-O-M bridged bis(carbene) complexes have been obtained from the extremely moisture sensitive metallacyclic carbene complexes and water (Scheme 3.8).[24]

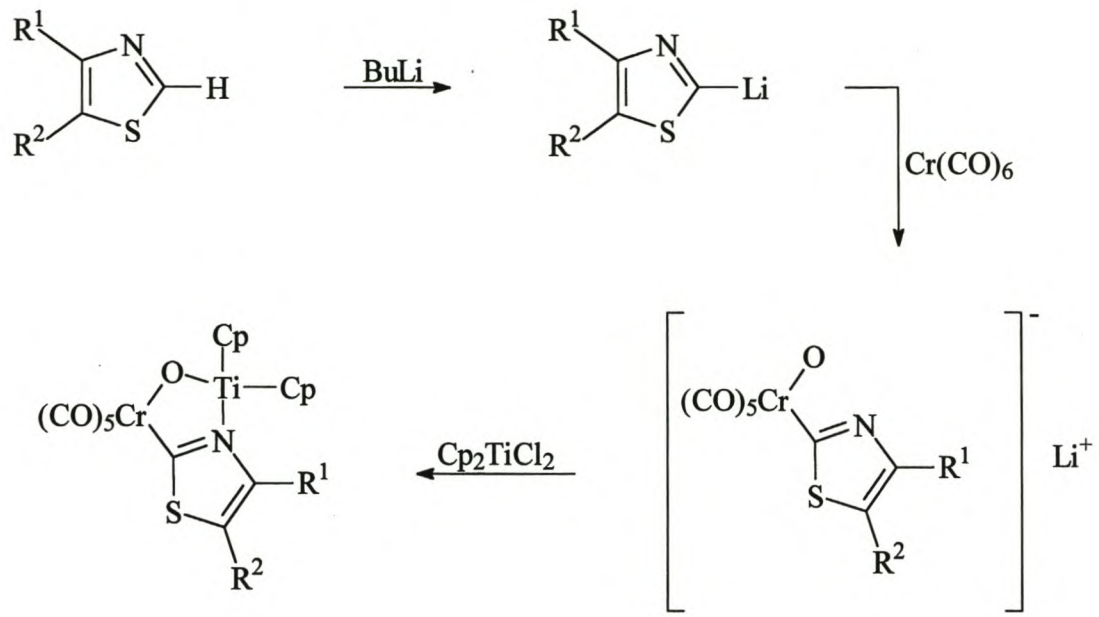
[22] (a) H. Yasuda, Y. Kajihara, K. Mashima and A. Nakamura, *Chem. Lett.*, 1981, 719. (b) G. Erker, K. Engel, J. L. Atwood and W. E. Hunter, *Angew. Chem.*, 1983, **95**, 506, 800.
[23] G. Erker, F. Sosna, R. Pfaff, R. Noe, C. Sarter, A. Kraft, C. Krüger and R. Zwettler, *J. Organomet. Chem.*, 1990, **394**, 99.
[24] G. Erker U. Dorf, C. Krüger and Y.-H. Tsay, *Organometallics*, 1987, **6**, 680.



Scheme 3.8

Bimetallic complexes containing Ti(III) have been prepared using a carbene complex as precursor (Scheme 3.9).[25] Thiazoles containing different substituents are deprotonated and added to metal carbonyls. The resulting carbene complex anion is a chelate and coordinates to bis(cyclopentadienyl)titanium dichloride in two coordination positions reducing the titanium(IV) to titanium(III). Work is still in progress to see whether this type of reaction can be extended to other group 4 and group 6 metals as well as other heterocyclic ligands.

[25] L. Van Niekerk, *M.Sc Thesis*, University of Stellenbosch, 1999.



$R^1 = R^2 = Me$

$R^1 = Me, R^2 = H$

$R^1\text{-}R^2 = C_4H_4$

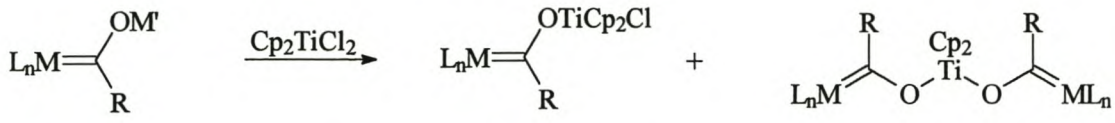
Scheme 3.9

(ii) Titanoxycarbene complexes and their role in organic synthesis

The presence of an electron deficient metal bound through oxygen to the carbene carbon atom offers the opportunity to control the carbene reactivity by steric and electronic variation of the Lewis acidic component. This means that metalloxy Fischer carbene complexes can be used to prepare compounds that cannot be prepared by the use of an alkoxycarbene complex.[26] The first complex of this kind, $(CO)_5Cr{=}C(CH_3)OTiCp_2Cl$, was synthesized by Fischer and Fontana.[27] Later the series was extended to include other metals and substituents on the carbene carbon. It was found that the bimetallic complexes formed exclusively if the reaction tempera-

[26] J. Barluenga and F. J. Fañanás, *Tetrahedron*, 2000, **56**, 4579.
[27] E. O. Fischer and S. Fontana, *J. Organomet. Chem.*, 1972, **40**, 159.

ture was kept below –40°C (Scheme 3.10).[28] Grubbs *et al.*[29] used the same method in 1988 as Raubenheimer and Fischer to prepare $(CO)_5Cr{=}C(Me)OTiCp^*_2Cl$ and $(CO)_5Cr{=}(Me)OZrCp^*_2Cl$.



M' = Li, NMe_4

L_nM = $(CO)_5Cr$, $(CO)_5Mo$, $(CO)_5W$, MeC_5H_5Mn

R = NMe_2, Me, Bu, Ph

Scheme 3.10

Titanoxycarbene complexes are stable in the solid state, but tend to decompose after a few hours in solution. X-ray structure determinations suggest a higher contribution of resonance form II than of I (Figure 3.3) in the structure of these complexes.[30]

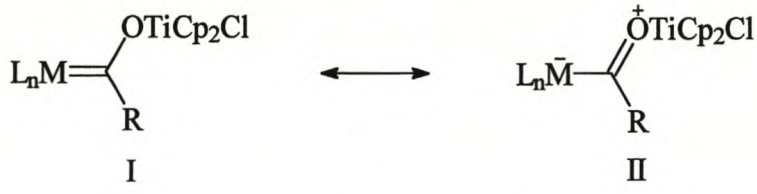
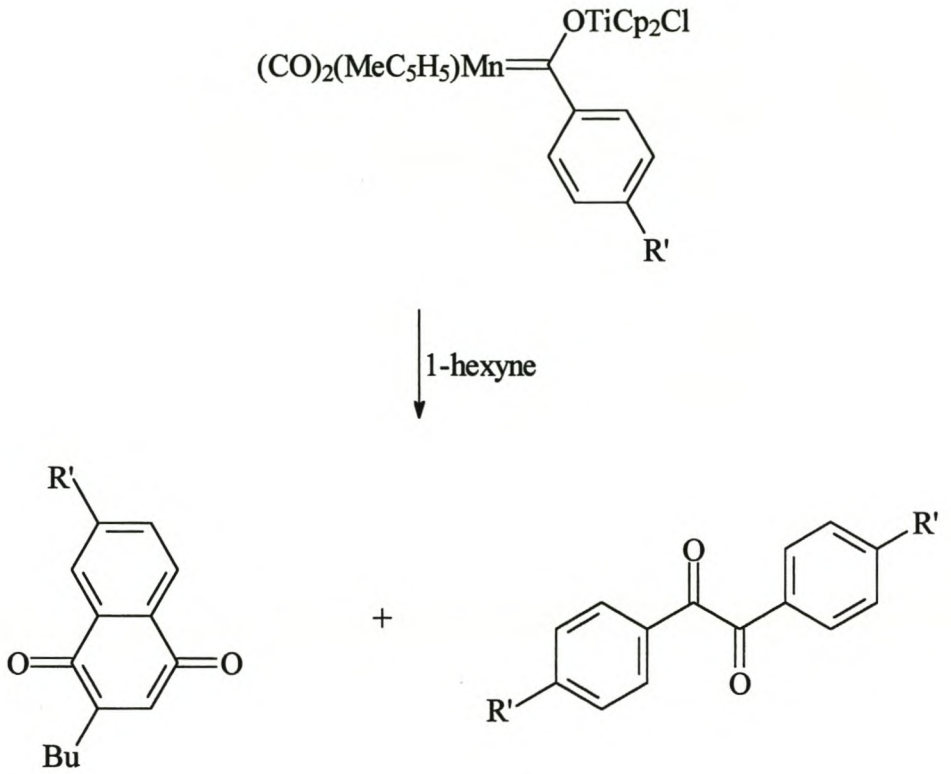


Figure 3.3: *Resonance structures for titanoxycarbene complexes*

Titanoxycarbene complexes can be reactive in benzannulation reactions under photolytic conditions or in refluxing of toluene (Scheme 3.11). In this reaction, the

[28] H. G. Raubenheimer and E. O. Fischer, *J. Organomet. Chem.*, 1975, **91**, C23.
[29] R. H. Grubbs, E. V. Anslyn and B. D. Santarsiero, *Organometallics*, **7**, 1988, 2137.
[30] M. Sabat, M. F. Gross and M. G. Finn, *Organometallics*, 1992, **11**, 745.

naphtoquinone derivatives are afforded in 28 – 30% yield in the presence of 10 equivalents of 1-hexyne followed by oxidative workup.[31]



Scheme 3.11

Alkoxymanganese complexes do not react under these conditions – proof that Fischer-type carbene complexes are activated by electron deficient metals.

(iii) Titanoxycarbene complexes in catalysis

The discovery by Ziegler[32] and Natta[33] that transition metals can be used as catalysts in alkene polymerisation sparked the polialkene industry. Today many active and selective heterogeneous catalysts are known and available in the plastics industry.[34]

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[31] B. C. Balzer, M. Cazanone, M. Sabat and M. G. Finn, *Organometallics*, 1992, **11**, 1759.
[32] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, 1955, **67**, 426.
[33] G. Natta, *J. Am. Chem. Soc.*, 1955, **77**, 1708.
[34] P. Pino and R. Mülhaupt, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 857.

Efforts have been made to find homogeneous catalysts for the polymerisation of α-olefins. Only with the discovery that partially hydrolized MAO can activate the group 4 transition metal metallocene complexes,[35] did homogeneous catalysis of α-olefins really came into its own. Since then a number of review articles and books have appeared on the topic, detailing the mechanism of the polymerisation and postulating active species and the like.[36] It has been found in our laboratory that it is possible to polymerise ethene and oligomerize 1-pentene using $(CO)_5W{=}C(Me)OTiCp_2Cl$.[37] The complex was compared to Cp_2ZrCl_2 and $Cp_2ZrCl(OMe)$ under identical reaction conditions. It was found that the carbene complex was the slowest catalyst in the polymerisation reactions, but that it gave by far the highest yield in the oligomerization reactions. It must be noted, however, that the reaction conditions were not optimised. Nevertheless, this study has shown the potential of metalloxy-carbene complexes in homogeneous catalysis.

3.1.3 Aims of this study

The aim of this study was to synthesize metalloxycarbene complexes and obtain at least one crystal structure of a complex that has not hitherto been studied by means of X-ray crystallography. It was decided to focus on complexes containing a phenyl substituent on the carbene carbon atom, because such a complex had not been synthesized in our laboratory to date. Other reasons to focus on titanoxycarbene complexes include their possible use as catalysts in the polimerization of α-olefins and their importance as intermediates in organic synthesis.[38]

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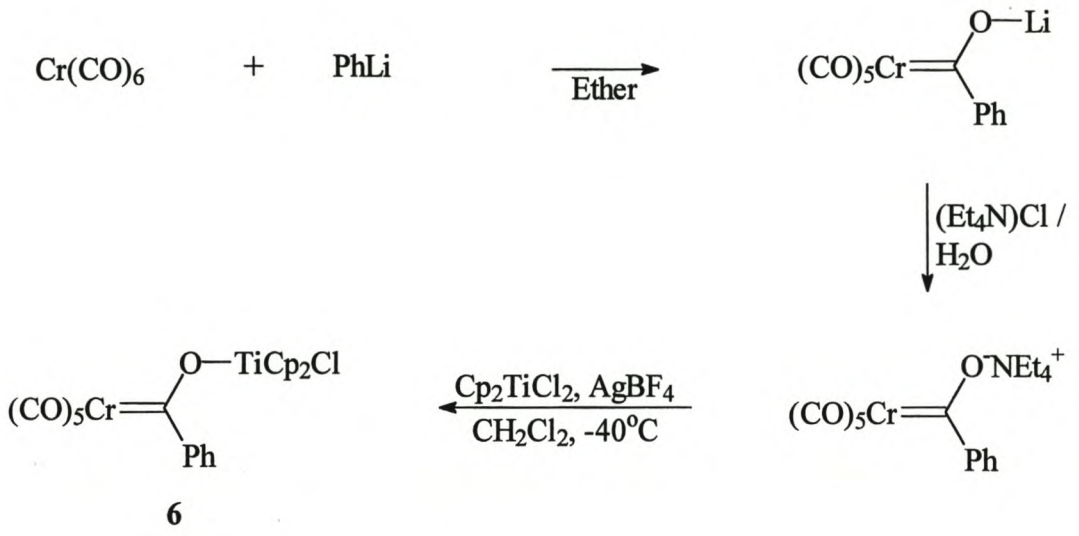
[35] H. Sinn, W. Kaminsky, H. J. Volmer and R. Woldt, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 390.
[36] (a) R. Mülhaupt, in *Ziegler Catalysts*, Springer-Verlag, Berlin, Heidelberg, 1995. (b) J. Boor, in *Ziegler-Natta catalysts and Polymerizations*, Academic Press, New York, 1991.

3.2 Results and discussion

3.2.1 Synthesis of complex 6

Complex **6** was prepared from $Cr(CO)_6$ in three stages (Scheme 3.12).



6

Scheme 3.12

In the first step phenyllithium was added to chromium hexacarbonyl in ether at room temperature to afford a lithium salt. The lithium salt was converted to the ammonium salt in water at room temperature. In the final step bis(cyclopentadienyl)titanium dichloride was added to the ammonium salt in CH_2Cl_2 at –40°C. Silver tetrafluro-borate was added to abstract a chloride anion from bis(cyclopantadienyl)titanium dichloride in order to ease the substitution of the ammonium cation by the oxophilic titanium. The complex was purified by means of column chromatography with silicagel as the stationary phase. The complex was subsequently cooled to –30°C in a

[37] A. Neveling, *M. Sc. Thesis*, University of Stellenbosch, 1999.
[38] M. A. Siera, *Chem. Rev.*, 2000, **100(10)**, 3591.

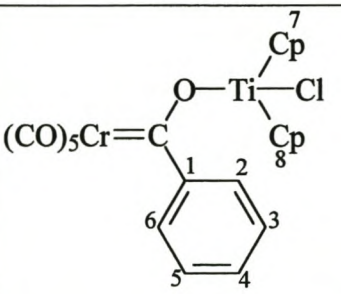
1:3 CH_2Cl_2/pentane solution yielding dark red single crystals. Complexes of a similar structure were synthesized before as discussed in the introduction to this chapter.

3.2.2 Spectroscopic characterization of complex 6

(i) NMR Spectroscopy

The ^1H NMR and ^{13}C NMR spectroscopic data for complex **6** is summarized in Table 3.1.

Table 3.1: *^1H and ^{13}C NMR spectroscopic data for complex **6***

Complex	
Solvent	CD_3COCD_3
H^7 and H^8	6.68 – 6.64 (10H, m)
H^2 and H^6	7.49 (2H, m)
H^3 and H^5	7.39 (2H, t, J = 1.68)
H^4	7.37 (1H, t, J = 1.75)
M=C	351.0
CO_{trans}	228.3
CO_{cis}	219.6
C^7 and C^8	120.6, 120.4, 121.8
C^1	155.0
C^2 and C^6	129.4
C^3 and C^5	124.9
C^4	131.7

In both the proton and ^{13}C spectra more than one peak is seen for the cyclopentadienyl groups. A possible explanation for this phenomenon lies in the many different configurations of the complex that can exist in solution (Figure 3.4). The presence of the Cp groups and the phenyl substituent inhibits free rotation to a certain extent and so there are differences in the intensities of these peaks.

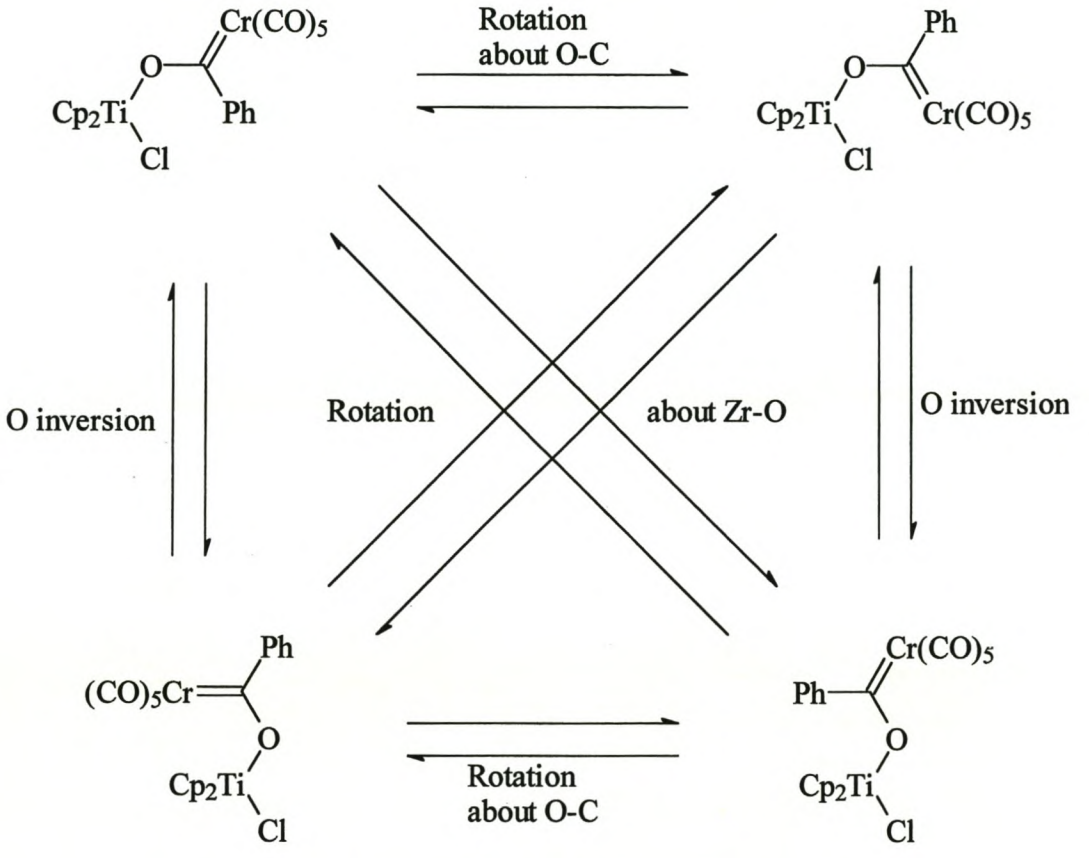
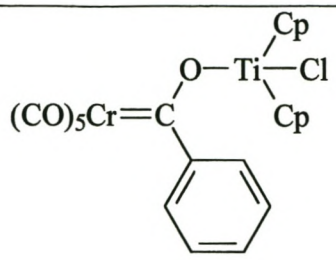


Figure 3.4: *Possible configurations for complex* ***6*** *in solution*

(ii) Mass Spectroscopy

The mass spectroscopic data for complex **6** is summarized in Table 3.2.

Table 3.2: *Mass spectroscopic data for complex* ***6***

Complex		
m / z	I[a]	Fragment ion
510	1	$[M]^+$
454	1	$[M-2CO]^+$
398	1	$[M-4CO]^+$
370	5	$[M-5CO]^+$
334	24	$[(CO)Cr{=}C(Ph)OTiCpCl]^+$
306	2	$[Cr{=}C(Ph)OTiCpCl]^+$
220	48	$[Cr(CO)_6]^+$
192	2	$[Cr(CO)_5]^+$
213	42	$[Cp_2TiCl]^+$
108	37	$[Cr(CO)_2]^+$
148	61	$[CpTiCl]^+$
80	58	$[Cr(CO)]^+$
65	14	$[Cp]^+$
52	100	$[Cr]^+$
28	61	$[CO]^+$

The molecular ion is at m/z = 510, as expected, although the relative intensity is very low. The base peak is that of $[Cr]^+$ at m/z = 52. The molecular ion splits into two fragments, one containing Cr and the carbonyl ligands (m/z = 220) and the other containing Ti and the Cp ligands (m/z = 213). The consecutive loss of the carbonyl ligands occurs as well, but the peaks are of a very low intensity.

(iii) Infrared spectroscopy

The ν(CO) data for complex **6** is summarized in Table 3.3.

Table 3.3: *ν(CO) vibration frequencies for complex* ***6***

ν(CO)/cm^{-1}		
$A_1(1)$	$A_1^{(2)}$	E
2 061 (m)	2 015 (st, sh)	1 975 (st)

As was said before, three infrared active bands (two A_1 and one E) are expected for pentacarbonyl compounds of which the symmetry of the CO-ligands is C_{4v}. With complex **6** this is indeed the case with the A_1 band occurring as a shoulder to the E_1 band at a higher frequency.

3.2.3 Structure of complex 6

The structure of complex **6** is shown in Figure 3.5 Throughout this discussion, structural features of complex **6** will be compared to similar structures as encountered in the literature and found in the Cambridge Crystallographic Data Centre (CCDC). For this purpose the reader is referred to the complexes shown and numbered in Table 3.4.

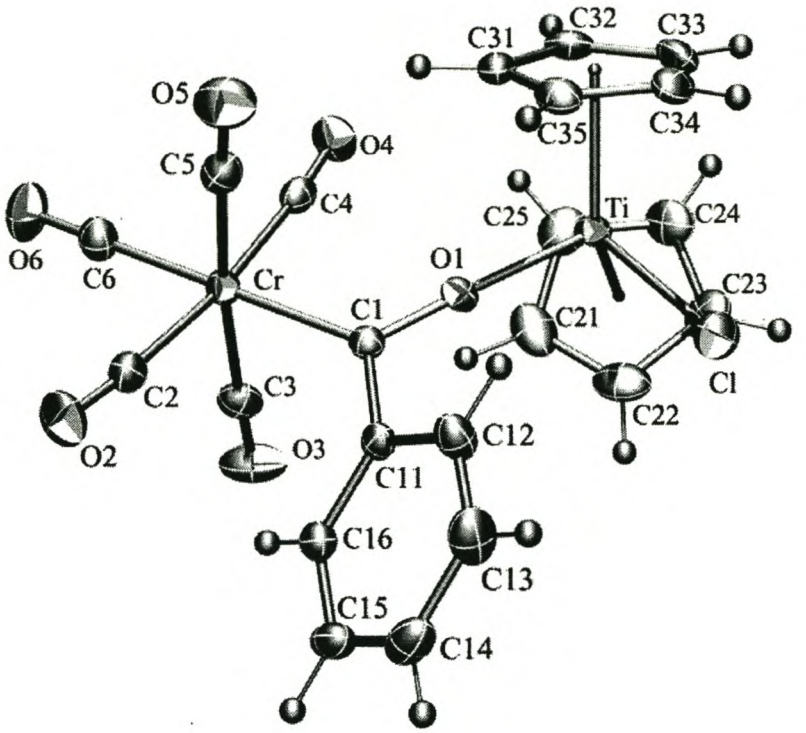
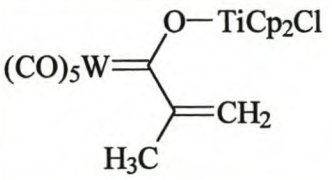
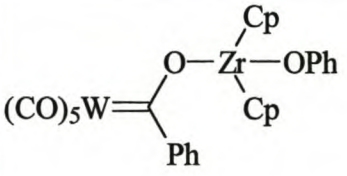
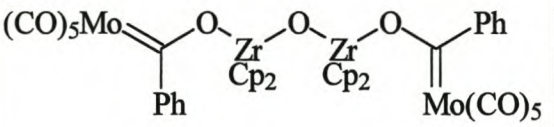
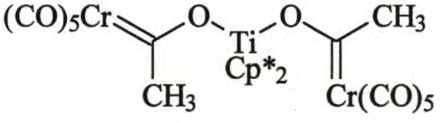


Figure 3.5: *Molecular structure of complex* ***6***

Table 3.4: *Comparable structures to complex* ***6*** *found in the CCDC*

Complex	Comments[a,b]
$(CO)_5W{=}C(CH_3)O{-}ZrCp_2Cl$	**i**[c] W-C6: 2.024(8), W-C1: 2.186(7) , C1-O1: 1.274(9) ,C1-O1-Zr: 178.0(5), Cp-rings are staggered
$(CO)_5Cr{=}C(CH_3)O{-}TiCp^*_2Cl$	**ii**[d] Cr-C6: 1.844, Cr-C1: 2.089, C1-O1: 1.286, C1-O1-Ti: 173.293, Cp-rings are staggered
$(CO)_5Cr{=}C(H_3C){-}CH_2{-}O{-}TiCp_2Cl$	**iii**[e] Cr-C6: 1.888 Cr-C1: 2.044, C1-O1: 1.268, C1-O1-Ti: 170.396, Cp-rings are eclipsed

Table 3.4: *Continued*

	**iv**[f] W-C6: 2.020, W-C1: 2.187, C1-O1: 1.265, C1-O1-Ti: 173.293, Cp-rings are eclipsed
	**iv**[g] W-C6: 1.989, W-C1: 2.188, C1-O1: 1.262, C1-O1-Zr: 166.031, Cp-rings are eclipsed
	**v**[h] Mo-C6: 1.987 Mo-C1: 2.195, C1-O1: 1.283, C1-O1-Zr: 175.611, Cp-rings are eclipsed
	**vi**[d] Cr-C6: 1.847, 1.861, Cr-C1: 2.107, 2.096 C1-O1: 1.271, 1.266, C1-O1-Ti: 150.008, 161.196, Cp-rings are staggered

a. Bond lengths in Å and angles in degrees

b. C1 = carbene carbon, O1 = carbene oxygen, C6 = carbon atom *trans* to carbene carbon

c. A. Neveling, *M. Sc. Thesis*, University of Stellenbosch, 1999.

d. E. V. Anslyn, B. D. Santarsiero, R. H. Grubbs, *Organometallics*, 1988, **7**, 2137.

e. M. Sabat, M. F. Gross, M. G. Finn, *Organometallics*, 1992, **11**, 745.

f. M. Sabat, K. A. Reynolds, M. G. Finn, *Organometallics*, 1994, **13**, 2084.

g. G. Erker, U. Dorf, R. Lecht, M. T. Ashby, M. Aulback, R. Schlund, C. Kruger, R. Mynott, *Organometallics*, 1989, **8**, 2037.

h. G. Erker, U. Dorf, Y.-H. Tsay, *Organometallics*, 1986, **6**, 680.

Selected bond lengths are summarized in Table 3.5. The carbonyl ligands of Cr are arranged octahedrally around the metal centre. (Refer to Table 3.6 for the relevant bond angles.) The Cr-$C_{carbonyl}$ bond lengths are more or less the same. (REfer to Table 3.5 for the relevant bond lengths.) The Cr-C6 bond length is slightly shorter [1.890(2) Å] than the average of the other Cr-$C_{carbonyl}$ bonds [1.899(2) Å], but the difference is not signifi- cant. Comparison to similar complexes has shown that there sometimes is a meaningful difference, but not always and that it cannot be correlated to any specific

structural feature. The Cr-C_{carb} bond is very long, at 2.062(2) Å and a look at Table 3.4 shows that the M-C_{carb} bond is invariably longer than 2 Å and substantially longer than an ordinary M-$C_{carbonyl}$ bond. The C1-O1 bond is very short at 1.297(2) Å which correlates with the C1-O1 bonds of the other structures which are all 1.2 – 1.3 Å.

Table 3.5*: Selected bond lengths for complex* ***6***

Cr-C1	2.062(2)	Ti-O1	1.9291(14)
Cr-C2	1.904(2)	Ti-Cl	2.3555(9)
Cr-C3	1.896(2)	Ti-C21	2.385(2)
Cr-C4	1.892(2)	Ti-C22	2.374(2)
Cr-C5	1.904(2)	Ti-C23	2.385(2)
Cr-C6	1.890(2)	Ti-C24	2.384(2)
C1-O1	1.279(2)	Ti-C25	2.354(2)
C2-O2	1.139(3)	Ti-C31	2.383(2)
C3-O3	1.140(3)	Ti-C32	2.367(2)
C4-O4	1.145(3)	Ti-C33	2.371(2)
C5-O5	1.140(3)	Ti-C34	2.406(2)
C6-O6	1.147(3)	Ti-C35	2.390(2)
C1-C11	1.509(3)		

This lengthening of the Cr-C1 bond and shortening of the C1-O1 bond is therefore a common feature of metalloxy carbene complexes and its occurrence can be explained by looking at the resonance structures for complex **6** (Figure3.6).

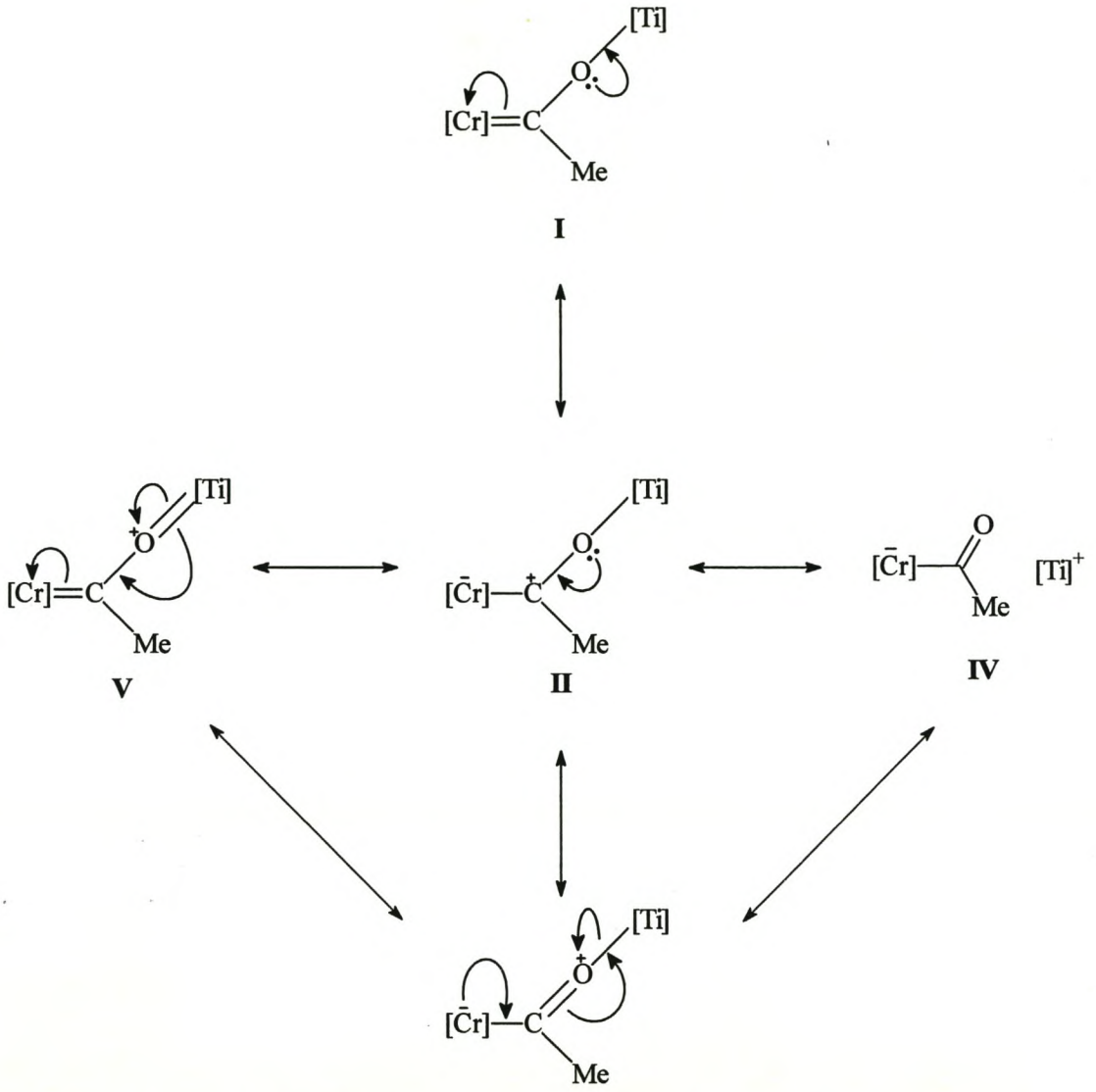


Figure 3.6: *Resonance structures for complex* ***6***

Although carbene complexes generally are represented as in structure I, this is not the most important resonance form. Structure II explains the electrophilic nature of the carbene carbon and its low resonance in ^{13}C NMR spectra. Structures III and IV shows why the C_{carb}-O1 bond is so short [1.297(2) Å]. Structures III and V show that it is possible for C_{carb}-O1-Ti to have a delocalised π-system. Structure IV has been used to explain the catalytic activity of the class of compounds in alkene polymerisation and oligomerisation reactions.[37]

Selected bond angles for Complex **6** are shown in Table 3.6.

Table 3.6: *Selected bond angles for complex* ***6***

C1-Cr-C2	93.12(9)	O1-Ti-C21	77.07(7)
C1-Cr-C3	88.01(9)	O1-Ti-C22	90.44(8)
C1-Cr-C4	93.16(9)	O1-Ti-C23	124.68(8)
C1-Cr-C5	85.19(9)	O1-Ti-C24	133.05(8)
C1-Cr-C6	179.22(9)	O1-Ti-C25	100.85(8)
Cr-C1-O1	123.49(14)	O1-Ti-C31	79.24(7)
Cr-C2-O2	175.2(2)	O1-Ti-C32	109.51(7)
Cr-C3-O3	177.4(2)	O1-Ti-C33	135.25(7)
Cr-C4-O4	175.28(19)	O1-Ti-C34	114.21(7)
Cr-C5-O5	176.2(2)	O1-Ti-C35	82.04(7)
Cr-C6-O6	177.3(2)	O1-Ti-Cl	96.14(5)
C1-O1-Ti	172.00(14)		

Due to the relative importance of π-bonding in structure V, the C_{carb}-O1-Ti atoms are almost linear [172.00(14)°]. This angle varies by about 30° for metalloxycarbene complexes (Table 3.4) and does not seem to be dependent on the metal involved or any other structural characteristics of the complexes. The partial negative charge of Cr is readily absorbed by the π-accepting CO-ligands. The titanium centre is coordinated to two Cp-ligands, the carbene oxygen and Cl. The O-Ti-Cl angle is 96.14(5)°. It is significantly different from the Cl-Ti-Cl angle in $Cp^*_2TiCl_2$ (92.9°).[39] The larger bond angle for complex **6** in comparison to $Cp^*_2TiCl_2$ is most likely due to nonbonding steric interactions between the Cl and the Fischer carbene phenyl group. The two Cp

[39] T. C. McKenzie, R. D. Sanner and J. E. Bercaw, *J. Organomet. Chem.*, 1975, **102**, 457.

ligands are almost eclipsed, unlike free Cp_2TiCl_2 where they occur in the staggered conformation. This is probably due to steric hindrance by the phenyl group because the eclipsing of the Cp or Cp* ligands occur as soon as the alkyl substituent on the carbene carbon atom is anything bigger than a methyl group. The phenyl group is directed away from the $TiCp_2Cl$-moiety to minimize steric hindrance.

The molecular packing of complex **6** in the unit cell as viewed along the a-axis is shown in Figure 3.7.

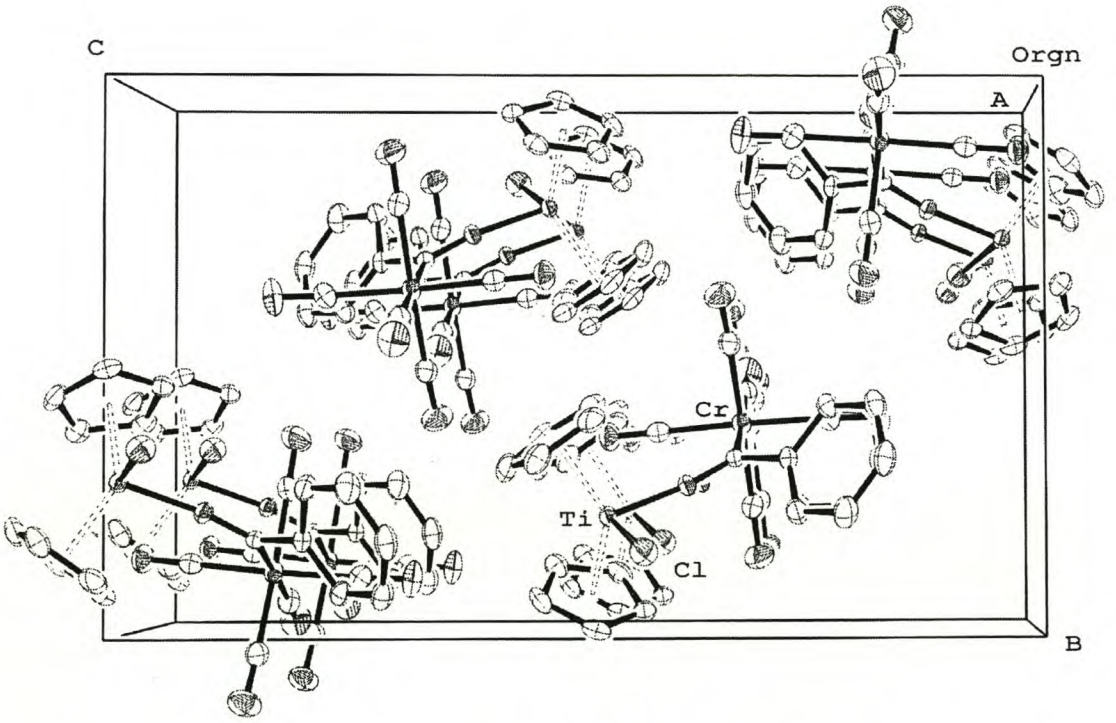


Figure 3.7: *Molecular packing of complex **6** in the unit cell*

There are eight molecules per unit cell. They are packed in layers in the crystal lattice. The layers alternate with regard to the orientation of the molecules. In every layer the molecules are packed in rows, with alternate rows being at different angles in order to fit in the phenyl groups and the cyclopentadienyl groups with minimum steric hind-

rance. This is a slightly different packing from that of complex **i** (Table 3.4), in which the molecules are also packed laying in different directions in alternate layers, but in each layer all the molecular orientations are the same. The crystal data and refinement particulars for the X-ray crystallographic determination of the structure of complex **6** are summarized in Table 3.7.

Table 3.7: *Crystal data and refinement particulars for complex* ***6***

Empirical formula	$C_{22}H_{15}ClCrO_6Ti$
Formula weight	510.69
Temperature	173(2) K
Radiation, Wavelength	Mo $K_{\alpha,}$ 0.71073 Å
Crystal system, space group	Monoclinic, P $2_1/c$
Unit cell dimensions	a = 8.434(2)Å, $\alpha = 90^o$, b = 12.258(3)Å, $\beta = 95.87(3)^o$ c = 20.637(4)Å, $\gamma = 90^o$
Volume	2122.3(7)$Å^3$
Z, calculated density	4, 1.589 g/cm^3
Reflections for cell parameters	12 565
Absorption coefficient	1.051 mm^{-1}
Absorption correction method	Semi-empirical (Scalepack)
T_{min}	0.730
T_{max}	0.842
F(000)	1 032
Crystal size	0.32 × 0.25 × 0.17 mm
Crystal Colour	Red

Table 3.7: *Continued*

Diffractometer type	EnrafNonius KappaCCD
Scan type	Area detector
Theta range for data collection	1.93 to 27.48°
Index ranges	$-10 \leq h \leq 9, -15 \leq k \leq 15, -26 \leq l \leq 26$
Reflections collected / unique	12 565 / 4 847 [R(int) = 0.0345]
Refinement method	Full-matrix least squares on F^2
Data / restraints / parameters	4 847 / 0 / 280
Goodness-of-fit on F^2 (S)	1.028
Final R indices [I > 2sigma (I)]	R1 = 0.0341, wR2 = 0.0804
R indices (all data)	R1 = 0.0528, wR2 = 0.0876
Weighting scheme	Calcw = $1/[\sigma^2(Fo^2)+(0.0408P)^2+0.8569P]$ where $P=(Fo^2+2Fc^2)/3$
Maximum shift/esd	0.001

3.2.4 Conclusions and possibilities for further study

Unfortunately, only one of the syntheses that were attempted was successful, but a very good crystal structure (R = 3.41%, see Table 3.7) was obtained. The complex does not seem to differ significantly in structure from similar complexes studied, but the packing in the crystal lattice is a bit different from that of complex **i** (Table 3.5).

To date, only one metalloxy carbene complex has been tested for catalytic activity, and it the light of the success obtained, it is definitely of paramount importance to test as many metalloxy carbene complexes as possible for activity in the catalysis of the polymerisation and oligomerisation of α-olefins.

Attempts have also been made to synthesize $(CO)_5Cr=C(Ph)TiCpCl_2$, but the product proved very difficult to purify and decomposed in solution. However, I do think it will be possible to prepare this complex, and other similar to it, provided a suitable way can be found to purify it.

Given the potential of metalloxycarbene complexes in organic synthesis, I also think that it is necessary to experiment with different ligands on the carbene carbon. A look in the CCDC has shown that to date only three different ligands that do not coordinate to the group 4 metal as well have been employed. Since the ligand on the carbene carbon is incorporated in the final organic product in syntheses utilizing metalloxycarbene complexes, it would be a very good idea to experiment with different organic groups.

3.3 Experimental

3.3.1 General

All reactions were performed under positive nitrogen pressure with a standard vacuum line and Schlenk techniques.[40] Glassware was dried at 120° for a minimum of twi hours and cooled under vacuum before use. Manipulations at low temperatures were done by placing the reaction flask in a propanol bath cooled by dry ice or liquid nitrogen.

All solvents were dried as follows: Dichloromethane, toluene pentene hexane and diethyl ether for two days minimum on potassium hydroxide and for at least two days on 3Å molecular sieves; THF for four days on potassium hydroxide. All the solvents were subsequently distilled in an inert atmosphere; dichloromethane over calcium

[40] D. F. Schriver, *Manipulation of Air-sensitive Compounds*, McGraw-Hill, New York, 1969.

hydride, pentane, hexane toluene, diethyl ether and THF over sodium wire, tetraglyme and benzophenone.[41] Separations by means of column chromatography[42] were done under a nitrogen atmosphere with kieselgel 60 (particle size 0.063 – 0.200 mm) from Merck as stationary phase. Double sided columns were used for low temperature separations. Before use, the stationary phase was washed with diethyl ether and dried under vacuum for 12 hours. Thin layer chromatography (Alugram Sil G/U_{154}) was used to follow the progress of reactions.

All ^{1}H and ^{13}C NMR spectra were recorded in deuterated acetone with a Varian VXR 300 spectrometer at 25°C. Mass spectra were recorded with a AMD 604 spectrometer. A Perkin Elmer 1600 Series FTIR was used to determine infrared spectra of solutions in dichloromethane.

All metal carbonyls, bis(cyclopentadienyl)titanium dichloride and methyllithium (1.6M in diethylether) were purchased from Aldrich and used without firther purification.

3.3.2 Synthesis of complex 6

$Cr(CO)_6$ (1.100g, 5.0 mmol) was suspended in diethyl ether (40 cm^3) and PhLi (6.50 cm^3, 0.8M in diethyl ether, 5.0 mmol)[43] dissolved in an additional 40 cm^3 diethyl ether was added over a period of 15 minutes while stirring at room temperature. The solution turns yellow immediately, and gradually turns to dark red. Stirring continued until all the $Cr(CO)_6$ has reacted (about two hours). The solvent was removed under

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[41] (a) D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemeicals*, Pergamon, Oxford, 1985. (b) A. Salzer in *Synthetic Methods of Organometallic and Inorganic Chemistry (Hermann/Brauer)*, **1**, (W. A. Harmann, A. Salzer: Eds), Georg Thieme, NY, 1996. (c) R. J. Errington, *Advanced Practical Inorganic and Metalorganic Chemistry*, Chapman & Hall, 1997.

[42] (a) W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.*, 1978, **43(14)**, 2923. (b) K. A. M. Kremer, P. Helquist, *Organometallics*, 1984, **3**, 1743.

[43] B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic chemistry, 5th Edition*, Longman Scientific & Technical, Essex, 1989.

vacuum and dried for an additional two hours. The lithium salt was dissolved in degassed water (40 cm^3) and filtered through Celite.

Et_4NCl (1.657g, 10 mmol) was dissolved in water (10 cm^3) and added to the filtered solution of the lithium salt. A bright yellow precipitate formed immediately. After stirring for 15 minutes, the solution was filtered and the precipitate dried for an hour. The precipitate was then dissolved in CH_2Cl_2 and filtered through $MgSO_4$. The solvent was removed under vacuum and yellow crystals of $(CO)_5Cr = C(Ph)O^-NEt_4^+$ were obtained (yield 1.864g, 75%).

The ammonium salt (1.864g, 3.75 mmol) was dissolved in CH_2Cl_2 (40cm^3). This solution was added over a time of 45 minutes to a suspension of Cp_2TiCl_2 (0.934g, 3.75 mmol) in CH_2Cl_2 (60 cm^3) at –40°C. The solution was stirred for 30 minutes at –40°C. $AgBF_4$ (0.730g, 3.75 mmol) was added and the reaction mixture was stirred for an additional 90 minutes at –40°C. After this the reaction mixture was allowed to reach room temperature, and the solvent removed by vacuum. The residue was extracted 5 times with 10 cm^3 portions of toluene and filtered through $MgSO_4$. The solution was dried by vacuum and the product was purified by means of column chromatography using a 3:1 CH_2Cl_2/hexane mixture as eluent. Upon drying of the solution, dark red powder of the product was obtained. This was dissolved in a 1:3 CH_2Cl_2/hexane mixture and cooled to –30°C for a week. Dark red single crystals of the product were obtained.

Yield (**6**). 1.148 g (45%)

3.3.3 Structure of complex 6

The crystal and molecular structure of complex **6** was determined by Dr. J. Bacsa (Department of Chemistry, University of Cape Town) and M. Esterhuysen

(Department of Chemistry, University of Stellenbosch). A clear crystal was mounted on a glass fibre and transferred to a Enraf-Nonius KappaCCD diffractometer. The data was collected with monochromatic Mo-K_α-radiation of wavelength λ = 0.71073Å and corrected for Lorenz and polarization effects. The position of the heaviest atom was determined by a Patterson synthesis and anisotropic displacement parameters were used for all the other atoms with the exception of the hydrogen atoms. The computer program SHELX-97 was used for the determination of the structure and the refinement of the atomic coordinates. Additional information can be obtained from M. Esterhuysen, department of Chemistry, University of Stellenbosch, Stellenbosch.